# Membrane Technology Prof. Kaustubha Mohanty Department of Chemical Engineering Indian Institute of Technology Guwahati

# Lecture-14 Concept of Osmosis and Reverse Osmosis Thermodynamic Analysis

Good morning students today is lecture 14 of module 5. In today's lecture will discuss about the concept of osmosis and reverse osmosis while discussing the concepts will take into account the thermodynamic analysis also and how the equations of osmosis and osmosis and reverse osmosis were actually derived based on the chemical potential difference concept. So you know the word osmosis is originated from the Greek word osmos.

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#### **Concept of Osmosis**

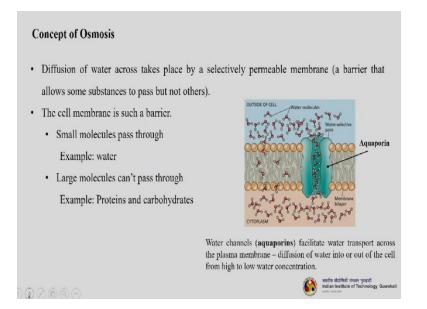
- The word 'osmosis' is originated from the Greek work 'osmos' which means 'to push'.
- · Osmosis, is a natural phenomenon, most commonly observed in plants.
- A plant cell is a semi-permeable membrane (water flows through the membrane but salts do not) with the living stuff inside in a salt solution.
- Water is drawn into the cell from outside because pure water moves across a semi-permeable membrane to dilute the high concentration of salt inside.
- · This is how water is drawn in from the ground when we water our plants.





Which means to push osmosis is a natural phenomenon mostly most commonly observed in plants. So the plant cell is a semi permeable membrane with the living stuff inside in a salt solution. So here in the in case of plant cell membrane the water flows through the membrane but salts do not. Water is drawn into the cell from the outside because pure water moves across a semi permeable membrane to dilute the high concentration of the salt inside. This is how water is drawn from the ground when we water our plants.

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Diffusion of water across takes place by a selectively permeable membrane a barrier that allows some substances to pass but not others. Now the cell membrane in such a barrier so 2 things are happening here so the small molecules will pass so water is a very small sized molecule so it will pass through whereas large molecules like proteins and carbohydrates it will not allow to pass through the membrane you can see the schema one schematic diagram here and this is giving you an example of the plant cell membrane actually.

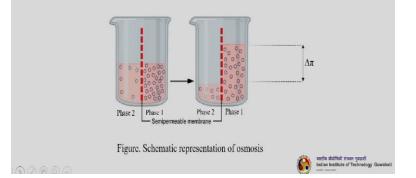
So these are called actually lipid bilayers here and this is water molecule you know how water is getting actual water molecule is getting actually transported inside the cell membrane. So this is the cytoplasm inside the cell and this is the outer side. So this is aquaporin these are called actually water channels. So what are aquaporin so aquaporin is a type of proteins now these are called water channels. So they facilitate water transport across the plasma membrane.

So you can see this water is getting transported here also in these areas also the liquid by layers in the plasma membrane also. However these aquaporin what is the their job is to transport these water molecules inside this membrane. So there is certain types of proteins. So which are helping which are binding to these water molecules and then they are getting them transported inside the cytoplasm. So they are called water channels and sometimes called pumps also and they are a specific type of proteins which are present in most of our plant cells.

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#### **Concept of Osmosis**

- An osmotic pressure arises when two solutions of different concentration (or a pure solvent and a solution) are separated by a semi-permeable membrane i.e. one which is permeable to solvent but impermeable to solute.
- Here, the membrane separates two liquid phases: a concentrated phase 1, and a dilute phase 2.



So an osmotic pressure arises when 2 solutions of different concentrations or a pure solvent and a solution is separated by semi permeable membrane. So one which is permeable to solvent but impermeable to solute. So let us see here this is one example of how osmosis is going to take place actually there are 2 separate because you can see inside which a membrane is placed so 2 different phases are existing.

So the phase 1 is the concentrator one that means, it has any one particular salute it may be salt it may be sugar anything which is present in that phase and the phase 2 which is here actually. So this actually the dilute phase. So it may be divided up any salute or at all any salute is present it is present in a very low concentration. So in between there is a semi permeable membrane, as you can see from this figure. So now we will try to understand actually what is happening.

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#### Concept of Osmosis

• Under isothermal conditions the chemical potential of the solvent in the concentrated phase (phase 1) is given by:

$$\mu_{i,1} = \mu_{i,1}^{\circ} + RT \ln a_{i,1} + V_i P_1 \tag{i}$$

· While, the chemical potential of the solvent in the dilute phase (phase 2) is given by:

$$\mu_{i,2} = \mu_{i,2}^o + RT \ln a_{i,2} + V_i P_2 \tag{iii}$$

The solvent molecule in the dilute phase have a *higher (more negative) chemical potential* than
those in concentrated phase. This chemical potential difference causes a flow of solvent molecule
from the dilute phase to the concentrated phase.

So under isothermal conditions I am trying to explain it using the chemical potential concepts. So under isothermal conditions the chemical potential of the solvent in the concentrated phase is given by mu i1 = mu i1 naught + RT ln a i1 +V i P 1. So mu i1 is the chemical potential of the pure substance 1 at standard temperature and pressure. So and the chemical potential of the solvent in the dilute phase is given by this equation.

Now the solvent molecule in the dilute phase has a higher or more negative chemical potential, then that of the concentrated phases. So this chemical potential difference causes a flow of solvent molecule from dilute phase to that concentrated phase. So let us go back and again see in this particular schematic diagram so you can see this the chemical potential in the phase 2 which is actually a water or a solvent having very less amount of solid present it is given by mu 1 and this is mu 2.

So what it says it was saying on the statement which I was reading earlier slide is that the chemical potential of this particular phase 2 which is the dilute phase is more negative. So that means there is a gradient to flow from here to here in this direction so this is due to the chemical potential direction gradient. So due to which the water from phase 2 which is dilute will flow to the concentrated phase.

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Concept of Osmosis
This process continues until osmotic equilibrium has been reached, i.e. when chemical potentials of the solvent molecules in both phases are equal:

μ<sub>i,1</sub> = μ<sub>i,2</sub>
(iii)

Combination of equation (*i*-*iii*) gives:

RT(lna<sub>i,2</sub> - lna<sub>i,1</sub>) = (P<sub>1</sub> - P<sub>2</sub>)V<sub>i</sub> = Δπ.V<sub>l</sub>
(v)

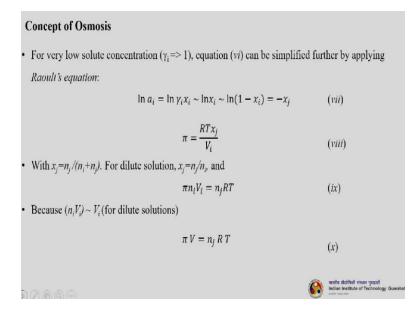
This hydrodynamic pressure difference (P<sub>1</sub>-P<sub>2</sub>) is called '*osmotic pressure difference*, Λπ'.
When only pure solvent is situated on one side of the membrane (phase 2), i.e. a<sub>i,2</sub> = 1, then the above equation can be re-written as:

π = - RT/V<sub>l</sub> lna<sub>i,1</sub>
(vi)

So this process will continue until osmotic equilibrium has been reached. That means when chemical potentials of the solvent molecules in both the phase 1 and phase 2 are equal. Now if you combine this all the equations of the chemical potential equations and we can write them in terms of activities and in terms of osmotic pressure that RT = pi a delta pi into Vi now what is this delta pi.

So, this delta pi is the difference between the pressure 1 and pressure 2 that means, the pressure of phase 1 minus the pressure of phase 2 so that is called the osmotic pressure difference delta pi. Now when only pure solvent is situated on one side of the membrane that is phase 2 if activity equals to 1 then above equation can be re written as that pi = -RT / VI a lna i 1. So whereas pi is the osmotic pressure of the phase 1.

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So for a very low concentrations, the activity coefficient usually stands to 1 so the earlier equation can be simplified by applying Roult's so we can write that  $\ln a i = \ln gama i x i$ . So that mean a i equals to here a is the activity. So equals to the activity coefficient into the mole fraction x i is the mole fraction and since activity coefficient stands to 1 for very low salute concentrations, so, you can write it  $\ln x i$  which is nothing but  $\ln 1 - x i = -x j$ .

So you can write that  $pi = RT \ge j / V$  i. So, further we can write that  $\ge j$  equals to the mole fraction of component j equals to the number of moles of j divided by number of moles of i plus more number of moles of J. And in case of dilute solutions, so, we can write further simplified it is the mole fraction of j equals to number of moles of j divided by number of moles of i. So hence we can write that pi n i V i = n j RT or for very dilute solutions n i V i is almost equals to V i so n I can be neglected because there is hardly any salute present in that.

So, number of moles of solutes would be neglected. So, we can write only V i. So hence this equation becomes pi V = n j RT. (Refer Slide Time: 08:13)

#### **Concept of Osmosis**

• And, since  $(n_i/V) = (c_i/M)$ , then

$$=\frac{c_j R T}{M}$$

(xi)

• This simple relationship between the osmotic pressure, ' $\pi$ ' and the solute concentration ' $c_j$ ' is called **van't Hoff equation**.

π

- It can be seen that the osmotic pressure is proportional to the concentration and inversely
  proportional to the molecular weight.
- If the <u>solute dissociates</u>, the equation:  $\pi V = n_i R T$  must be modified.
- When dissociation occurs the number moles increases and hence the osmotic pressure increases proportionally.
- Whereas, in case of association the number of moles decreases as does the osmotic pressure.

Again you know n j / V = c j / M. So c j is the concentration of the solute and divided by M is the molecular weight. Hence the above equation again reduces that pi = c j RT / M. Now you know this is the relationship between the osmotic pressure and the concentration and it is called the van't Hoff equation. This is one of the most important equations that will come across whenever you talk about osmosis or reverse osmosis.

Now it can be seen that the osmotic pressure is proportional to the concentration and inversely proportional to the molecular weight from this particular equation you can see the osmotic pressure is directly related to the 2 important parameters. One is the concentration of the solute another is the molecular weight. Now it is directly proportional to the concentration of the solute and inversely proportional to the molecular weight.

So what happens many times whenever there is a solvent in the salt or solutes are present so some of the solutes dissociates. Now when the solution dissociates then we can write that pi V = n j RT that should be actually that equation kind of equation should be modified now why because when dissociation occurs the number of moles of that particular saluted increasing and hence osmotic pressure also increases proportionately. Now here is in case of association the number of moles decreases because they are associating with themselves and so does as does the osmotic pressure also.

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#### **Concept of Osmosis**

- · The osmotic pressure difference in microfiltration and ultrafiltration application are quite low, whereas it has to be taken in account in reverse osmosis.
- · In this case the osmotic pressure can be expressed by a virial expansion:

$$\pi = \frac{RT}{M}c + Bc^2 + \dots$$
(xii

(xiii)

- · Often more simple exponential relationship has been applied for macromolecular solutions:  $\pi = a.c^n$
- Here, 'a' is a constant and 'n' is an exponential factor with value greater than 1. Hence if the concentration is high the osmotic pressure can be high as well and this concept may be used to describe the 'concentration polarisation' i.e. although the osmotic pressure of the bulk solution is low. The concentration at the wall may have increased drastically as does the osmotic pressure. अरतीय सीयोगिकी रांख्यम गुवाहारी Indian Institute of Technology Gu

So, the osmotic pressure difference in microfiltration and ultrafiltration and application are quite low whereas it has to be taken into account in reverse osmosis. In this case automatic pressure can be expressed mostly viavirial expansion. So you can write pi = RT / Mc + Bc square + cc cube like that it will go on it is a real expansion equation actually and more simple exponential relationship also can be applied for example for macromolecular solutions.

So you can write pi = a c to the power of n here a is the constant and n is an exponential factor with a value greater than 1. Hence, if the concentration is high osmotic pressure can be high. So this particular request says that when the concentration is high this equation says that osmotic pressure is directly related to the concentration of course to a term raised in so if the concentration is high the osmotic pressure can be high and this concept may be used to describe the concentration polarisation.

So if you remember, when we were discussing our introductory classes I think lecture 1 or 2 I was telling you about concentration polarisation which is supposed to be one of the problem associated with any membranes is phenomena actually will make you understand that how is still a concentration polarisation and it is happening. So although osmotic pressure of the bulk solution is very low. The concentration at the wall may have increased drastically as does the osmotic pressure.

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#### Determination of osmotic pressure

- The thermal movement of a solute molecule within a solvent is over dampened by the solvent molecules that surround it.
- The solute molecule is wholly determined by fluctuations of the thermal collisions with nearby solvent molecules.
- However, the average thermal velocity of the solute molecule is the same had it been free in a
  gas phase, without nearby solvent molecules.
- Whenever, a solute molecule is blocked by the membrane it will transfer momentum to it and, therefore generate pressure on it.
- Since the velocity is same as free molecule, the pressure will be same as the pressure of an ideal gas of the same molecular concentration.

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So let us understand how will determine the osmotic pressure. Now the thermal movement of a solute molecule within the solvent is over dampened by the solvent molecules that surround it. The solute molecule is wholly determined by fluctuations of the thermal collisions with nearby solvent molecules. However the average thermal velocity of the solute molecule is the same had it been free in a gas phase without nearby solvent molecules. Now whenever a solute molecule is blocked by the membrane.

It will transfer momentum to it and therefore, generate pressure in it. So, this is how you will try to now you can understand that actually the pressure is getting generated when the solid molecules are getting deposited on the surface of the membrane thereby building the concentration polarization layer. Since the velocity is same as free molecule the pressure will be same as the pressure of an ideal gas of the same molecular concentration.

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# Determination of osmotic pressure Hence, the osmotic pressure 'π' is given by van't Hoff formula, which is identical to the pressure formula of an ideal gas: π = π/V<sub>w</sub> RT (i) where, 'n' is the number of kg mol of solute, V<sub>w</sub> the molar volume of pure solvent water (in m<sup>3</sup>) associated with the n kg mol of solute, R is the gas constant (82.057x 10<sup>3</sup> m<sup>3</sup>.atm/kg mol.K), and T is the absolute temperature (in K). The osmotic pressure doesn't depends on the solute type, or its molecular size, but only on its molecular concentration.

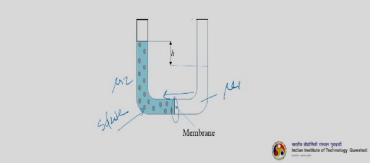
Hence osmotic pressure is given by the van't Hoff formula, which is identical to the pressure of an ideal gas as you know, we have already discussed that  $pi = n / V \le RT$ . So here n is the number of kg mol of solute (())(12:24) molar volume of pure solvent in meter cube associated with n kg mol of the solute R is the gas constant and T is the absolute temperature in Kelvin but the osmotic pressure does not depend on the solute type this is very important to understand.

So, osmotic pressure has nothing to do with the solute type or molecular size, but it only depends upon its molecular concentration how much concentration is present based on that actually the osmotic pressure will be either low or it will be high. It has nothing to do with what type of solute is and what is its molecular size. So the figure below shows the connected vessel separated by a semi permeable membrane.

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#### Determination of osmotic pressure

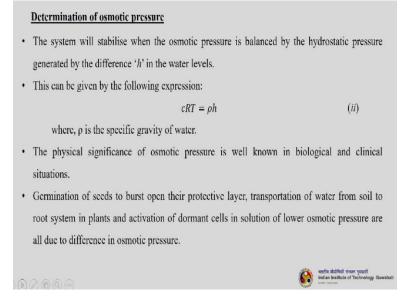
- · The figure below shows a connected vessel separated by a semi-permeable membrane.
- If there is only water in the device, the level will be same in both arms.
- When the solute molecules are added to one arm, water will start to flow into it, so that its level will rise at this arm, and fall out of other arm.



There is a membrane here. And if there is only water in the device, the level will be same in both arms. However when salt molecule solid molecules are added to one arm so here we are adding salt molecules. So water will start to flow into it. So that means the movement of water is happening from here to here in this direction. Now as you understand that again we have discussed this ministry for here the chemical potential of this phase it is very negative than this particular phase here.

So that is why that there is a gradient in chemical potential exist from this sides to that side so from right to left so your water is water will flow into the concentrated phase.

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The system will stabilise when the osmotic pressure is balanced by the hydrostatic pressures generated with a difference in the water levels. So the system or system will stabilise when the hydrostatic head n osmotic pressure will balance themselves. So this can be given by the following expression cRT = ph were p is the specific gravity of the water. So the physical significance of osmotic pressure is well known in biological and clinical situations.

So one of the classic examples that you must have seen or know all that how the germination of seeds takes place. So the germination of seeds to bust upon their protective layer transportation of water from soil to root system in plants activation of dormant cells in solution of lower osmotic pressure are all due to the difference osmotic pressure.

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Determination of osmotic pressure

 The table below shows the osmotic pressure of various dilute aqueous solution of NaCl at 25°C;

gmol NaCl kg H <sub>2</sub> O	Density (kg/m <sup>3</sup> )	Osmotic pressure (atm)
0	997.0	0 1
0.01	997.4	0.47
0.10	1001.1	4.56
0.50	1017.2	22.55
1.00	1036.3	45.80
2.00 🗸	1072.3	96.20

So this particular table shows the osmotic pressure of various dilute aqueous solution of sodium chloride at 25 degrees centigrade. So, this will just make you understand that what is the osmotic pressure at a particular salt solution. So, you can see 0 when there is no salt sodium chloride you can saw the osmotic pressure is 0 you add just 0.01 gram mols for kg you see the osmotic pressure becomes 0.47 he keep on adding you reach 2 gram mols of sodium chloride per kg of water you see that osmotic pressure has become 96.2 atmosphere .

This will understand that when you are increasing a salt solution your osmotic pressure also getting increased.

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#### **Concept of Osmosis**

Thermodynamic consideration of osmosis

- · Reversibility is a fundamental idea of thermodynamic.
- Osmosis, is a reversible thermodynamic process.
- This implies that the direction of water flow through the membrane can be reversed at any
  moment by proper control of external pressure on the solution.
- · Osmosis phenomenon can be explained in the light of Gibbs free energy

G = H - TS (iii) where, G is Gibb's free energy, H is enthalpy, T is absolute temperature, and S is entropy.

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So let us try to understand little deep about the thermodynamic considerations of osmosis. So you know that, reversibility is a fundamental idea of thermodynamics and osmosis is a reversible thermodynamic process. So that was because when you are applying a pressure which is more than that of the osmotic pressure you can reverse do the reverse law which is of course knowledge reverse osmosis and we are going to discuss in today's lecture about that also.

So this implies that the direction of water flow through the membrane can be reversed at any moment by proper control of the external pressure. So, we need to suck we need some external pressure to reverse the flow against its chemical gradient of course. So osmosis phenomenon can be explained in the light of Gibbs free energy let us try to understand using the Gibbs free energy concept. So you know that G = H - TS where g is the Gibbs free energy, H is the enthalpy, T is the absolute temperature and S is the entropy.

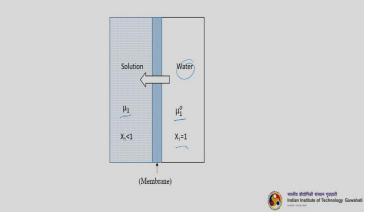
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Thermodynamic consideration of osmosis	
• Again: $H = E + PV$	( <i>iv</i> )
· In differential form, these equations can be expressed as	
dG = dH - TdS - SdT $dH = dE + PdV + VdP$	(v)
df = dE + PdV + VdP - TdS - SdT	( <i>vi</i> )
- Chemical potential $(\boldsymbol{\mu})$ is essentially a driving force expressed	l as a result of change in
composition of the system.	
• The standard chemical potential is defined as the free energy per	mole of substance formed,
consumed or transferred from one phase to another in its standard	state, which corresponds to
l atm pressure at particular temperature (usually at 20 °C).	
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So again we can write enthalpy in the terms of E + PV in differential form these equations can be expressed as dG = dH - Tds - SdT dH = dE + PdV + VdP and we can write that dG = dE + PdV. So it is just combining from the above equation plus VdP - TdS - SdT. So chemical potential now will try to introduce the chemical potential concept into this Gibbs free energy equations.

So chemical potential is essentially a driving force as a result of changing composition of the system. And the standard chemical potential is defined as the free energy per mol of substance formed consumed or transferred from one phase to another in its standard state, which corresponds to one osmotic pressure at a particular temperature usually a 20 degree centigrade. So, the figure below shows that 2 chambers are separated by a semi permeable membrane (**Refer Slide Time: 17:26**)

• The figure below shows that two chambers are separated by a semi-permeable membrane. The right one contains a very dilute solution or the pure solvent and other contains a solute dissolved in the solvent.



The right one contents a very dilute solution. So this is water or the pure solvent we can say and the other contains a solute dissolved in the solvent. The chemical potential of this phase the dilute phase is mu 1 naught the chemical potential of the concentrated phase is mu 1 he had the mole fraction = x = 1 here it is less than 1.

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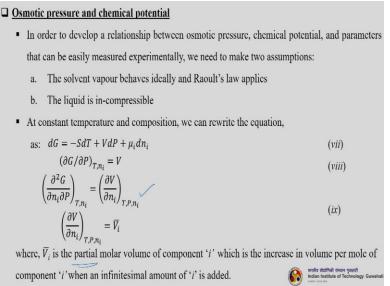
- The pure solvent in right compartment containing a mol fraction of water (x<sub>i</sub>), would have chemical potential (μ<sub>1</sub><sup>0</sup>), while the solution compartment with a mol fraction of water less than 1, would have a lower chemical potential of μ<sub>1</sub>.
- <u>The highest form of energy of water is when it is in pure state</u>. Adding any material (or solute, here salt) to it results in increase in its entropy.
- In other words, the chemical potential of water in a solution is always lower than when it is in pure state.
- This indicates that the water in the right compartment has a greater chemical potential than the water in the left compartment.
- Since, the two compartment are separated by a semi-permeable membrane (i.e. the membrane is
  only permeable to the water and not to the solute), the movement of solvent from the dilute
  solutions to more concentrated solution takes place.

The pure solvent in the right compartment containing a mole fraction of water x 1 would have chemical potential mu 1 naught that will since it is pure it is divide of any salute. So obviously it is the chemical potential can be taken as their standard chemical potential which is given for the pure substances or pure solutions solvents so while the solution compartment with a mole fraction of water less than 1 would have a lower chemical potential of mu 1.

So the highest form of energy of water is when it is in pure state so, adding any material for any salute this for example salt or sugar, it results in increasing its entropy. In other words the chemical potential of water in a solution is always lower when it is in its pure state. So this indicates that water in the right compartment has a higher or greater chemical potential than water in the left compartment seems the 2 compartments are separated by semi permeable membrane.

There is a membrane is only permeable to the water and not to the solute the movement of solvent from dilute solutions to concentrator solution which takes place. So the movement is taking place this is given by this particular direction.

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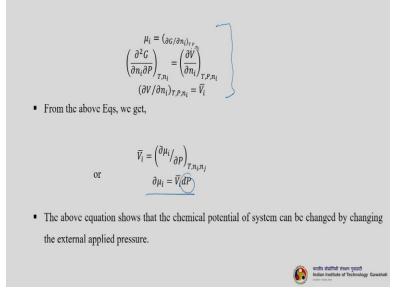
So in order to develop a relationship between osmotic pressure chemical potential and parameters that can be easily measured experimentally we need to make 2 assumptions. So the 2 assumptions are that the solvent vapour behaves ideally and Raoult's law applies. So this is where assuming and the liquid is incompressible. So, assuming after assuming these 2 things so we can write at constant temperature and composition the gives free energy equals.

And the changes in (())(19:49) energy equation = -SdT + VdP + mu i dn i. So you know that del G / del P at constant temperature and number of mols equals to V the molar volume and we can express Gibbs free energy in the Dell form in terms of V for in this equation and you know that

del V / del and del ni, ni is the number of mols of solute i at constant temperature pressure and constant mols equals to V i.

So V i bar is the partial molar volume of the components of partial that is where the bar is there i which is the increasing volume per mol of the component i when an infinitesimal small amount of i is added so very small amount of i is added then only this equation is (())(20:36) actually.

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So again I will rewrite these equations just for the understanding from these 3 equations which are already given in the earlier slides. So you can rewrite that V i = del mu i / del P at constant temperature at constant mols of salute i equals n j. So del mu y = V i into dP. So the above equation shows that chemical potential of a system can be changed by changing the external applied pressure.

So you can see that mu i is directly related to the partial molar volume as that of the pressure. So you change in pressure your chemical potential of a system will be changed. So furthermore since a solution and its vapour are in equilibrium. We can also substitute the ideal gas law into the equation to obtain d mu i = RT dP I / P i. So the above equation states that a change in vapour pressure due to a change in the concentration of this salute or solvent is happening.

So the following boundary conditions can be used while we integrating the above equation we need to integrate this. So you put ideal solutions we use this particular boundary conditions when

mu = mu i naught when p = p naught and mu = mu 1 when P = P. So when you integrate this will you will get this equation mu i – mu i naught = RT ln P / P naught.

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• For aqueous solution, *i* = 1 (for water)

 $(\mu_1^o - \mu_1) = -RT \ln (P/P^o)$ 

• Substituting,  $P = X_I P^0$  into above equation, we get:

$$\left(\mu_1^o - \mu_1\right) = -RT \ln X_1$$

- In physical terms, the above equation states that since the mole fraction of water in a solution is always less than 1, the term (*In X<sub>1</sub>*) is negative. This eventually means the right hand side of above equation is always positive quantity.
- Thus,  $\mu_1^0 > \mu_1$  and the natural phenomenon will be for water to flow from the pure water side to the solution side.
- To overcome this natural tendency, the chemical potential difference has to overcome by applying external pressure to the solution side.

And for aqueous solutions i = 1 for the water phase. So mu 1 naught - mu 1 = - RT ln P / P naught. So substituting P = x 1 P naught into the above equation will get mu 1 naught - mu 1 = - RT ln x 1. In physical terms, the above equation states that the mole fraction of water in a solution is always less than 1 the term ln x 1 this is always becoming negative. Hence that is a negative sign is incorporated to counterbalance the negative sign.

This eventually means the right hand side of above equation is always positive quantity. So thus mu 1 naught greater than mu 1. And the natural phenomenon will be for water to flow from the pure water side to the solution side or the concentrator side. To overcome this natural tendency the chemical potential difference has to be overcome by applying an external pressure to the solution side then that becomes actually reverse osmosis we are going to discuss that.

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The governing equation will be combination of the following equation:

$$\mu_1^o - \mu_1 = -RT \ln X_1 + \int_{P_0}^{P^*} \bar{V} dx$$

where,  $P^*$  is the external pressure and  $P_0$  is a standard pressure.

- By definition, the pressure applied is such that  $(\mu_1 \mu_1^o = 0)$  is called, osmotic pressure.
- Assuming, the liquid to be in-compressible, so that V can be taken out from the integral sign (refer to the above equation).

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or,

V_{1}\pi = -RT \ln X_{1}
\pi = \frac{RT}{\overline{V_{i}}} \ln X_{i}
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So the governing equation will be combination of the following equation mu 1 naught – mu 1 = RT ln x 1 + (())(23:12). So let P star is the external pressure P naught is the standard pressure by definition the applied pressure he says that mu 1 - mu 1 naught = 0 which is called the osmotic pressure. So assuming that liquid to be incompressible the V can be taken out from the integral sign. So he can write V 1 pi = - RT ln x 1 or pi = RT / V i bar ln x i.

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- (Refer Slide Time: 23:39)
  - The above equation is the thermodynamic relationship or osmotic pressure, derived using only two assumptions: <u>ideal solution behaviour</u>, which holds true only for very dilute solutions and the <u>liquid is incompressible</u>, which is valid only at relatively low pressure.
    Van't Hoff had independently developed a correlation for osmotic pressure: *π* = *n*<sub>2</sub> *RT*where, *n*<sub>2</sub> is molar concentration of the solute in moles per litre of the solutions.

    The above equation can be derived from more rigorous equation by rather extreme approximations: since X<sub>1</sub> is the mole fraction of water, *X*<sub>1</sub> + *X*<sub>2</sub> = 1 *X*<sub>1</sub> = 1 - *X*<sub>2</sub>

The above equation is the thermodynamic relationship or the osmotic pressure derived using only 2 assumptions. First is that ideal solution behaviour, which holds true only for very dilute solutions. And the second one is that the liquid is incompressible which is valid on late relatively low pressure. Van't Hoff had independently developed a correlation for osmotic pressure the question is pi = n 2 RT, but n 2 is the molar concentration of the solute in moles per liter of the solutions.

Now the above equation can be derived for more rigorous equation from more rigorous equation by rather extreme approximation since x 1 is the mole fraction of water, so we can write x 1 + x2 = 1 or x 1 = 1 - x 2.

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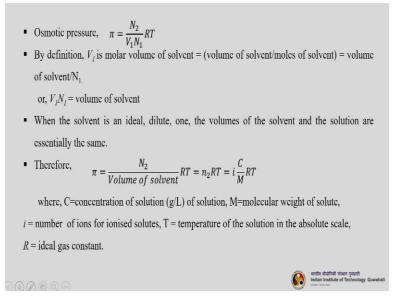
- The above equation is the thermodynamic relationship or osmotic pressure, derived using only two assumptions: <u>ideal solution behaviour</u>, which holds true only for very dilute solutions and the <u>liquid is incompressible</u>, which is valid only at relatively low pressure.
- · Van't Hoff had independently developed a correlation for osmotic pressure:

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\pi = n_2 RT
where, n_2 is molar concentration of the solute in moles per litre of the solutions.
• The above equation can be derived from more rigorous equation by rather extreme approximations: since X_1 is the mole fraction of water,
X_1 + X_2 = 1
X_1 = 1 - X_2
```

When x 2 is very less than 1 or less than 1. So by definition, we can write  $\ln 1 - x 2 = -x 2$  or  $\ln x 1 = -x 2$  or x 2 becomes N 2 / N 1 + N 2. So when n is the number of mols of component 1 or 2 since n 2 is less than 1 the above question can be re written as x 2 = N 2 / N 1.

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So the osmotic pressure can be written as pi = N 2 / V 1 N 1 RT. So by definition V 1 is the molar volume of the solvent that is volume of solvent for moles of solvent equals to volume of solvent / N 1 or V 1 N 1 = volume of the solvent. So when the solvent is an ideal dilute one, the volumes of the solvent and the solution are essentially the same. So therefore we can write pi = N 2 / volume of solvent into RT is nothing but n 2 RT all or we can write i C / M RT where C is the concentration of the solution grams per liter and M is the molecular weight of the solute.

Now i is the number of ions for ionized salutes T is the temperature of the solution in the absolute scale and R is the ideal gas constant. So pi it can be written as i C / M RT.

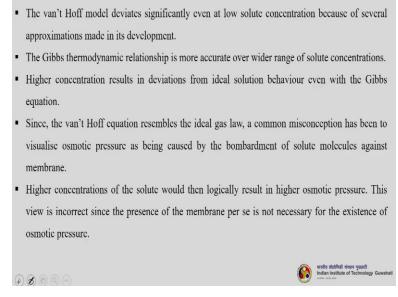
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Concentration	Molality	C	Smotic pressure (at	n)
(% w/w)		Van't Hoff equation	Gibbs model	Experimental data
25.31	0.991	20.3	26.8	27.2
36.01	1.646	30.3	47.3	(47.5)
44.73	2.366	39.0	72.6	72.5
52.74	3.263	47.8	107.6	105.9
58.42	4.108	54.2	143.3	144.0
64.58	5.332	61.5	199.0	204.3
			V	

So, this table will make you understand the relative accuracy of the 2 models predicting the osmotic pressure. So this is the concentration of the concentration of the solute this is the molality the second column and the fifth column here this these are experimental data, you can see what is the osmotic pressure that is calculated from the van't Hoff equation this column and that is from the Gibbs model.

You can see this van't Hoff equation the values are little off track and the Gibbs model actually they are predicting quite accurate you can see the value 47.5 47.3 105.9 107.6 you can see that Gibbs model and experimental data are matching almost very they are very close to each other that data's by the van't Hoff equation is little slight cut off that is because of the assumption. The 2 assumptions which were considered while deriving this equation.

#### (Refer Slide Time: 26:35)



So the van't Hoff model deviates significantly even at low solute concentration because of several approximations. The Gibbs thermodynamic relationship is more accurate over wider range of solute concentrations higher concentration results in deviations from ideal solution behaviour, even with the Gibbs equation since the van't Hoff question resembles the ideal gas law a common misconception has been to visualize osmotic pressure is being caused by the bombardment of solute molecule against membrane.

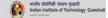
So, higher concentration of the solute would then logically result in higher osmotic pressure. This view is incorrect since the presence of the membrane per se is not necessary for the existence of osmotic pressure. So, try to understand that the membranes presence has no meaning when we are defining osmotic pressure. Osmotic pressure will come into picture whenever there is a salute salts anything that is present in a solvent.

If there is a pure water there is of course no osmotic pressure is coming into picture unless until we separate it from another solvent which is having here this one some salt separated by a membrane . So, the inherent meaning from this particular sentence is that membrane has no role when we are talking about osmotic pressure. How about it what it is doing is that it is helping since it is a semi permeable membrane. It is helping in passing the water from the dilute phase to the concentrated phase this is what it is doing thereby not allowing. Since it is semipermeable thereby not allowing the solutes to pass from the other phase to that dilute phase.

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- The physical significance of osmotic pressure in biological and clinical situations is well known: the osmotic pressure difference causes germination of seeds to burst open their protective coat.
- This causes drawing of water from the soil to the root system of plants, and can burst open by immersing them in a solution of much lower osmotic pressure.
- As far as membrane processing is concerned, its major significance lies in the fact that the
  external pressure must be applied for significant permeate flux must be higher than the osmotic
  pressure of the solution.
- The basic relationship between applied pressure (by pump), osmotic pressure, and the flow of solvent through the membrane is like many transport processes, expressed in terms of flux and the driving force and resistances.

#### 



So the physical significance of osmotic pressure in biological and clinical situations is well known. So the osmotic pressure difference causes germination we just discussed in few slides back also. So when the germination of Gibbs is happening now, what is happening the seed which seed is taking the water inside the cell but you can think and about the aquaporin protein which I sought or the water channels or the water pumps, so, they are helping by to take the water from the outside to inside the cell?

So then the water volume is actually increasing since the water is volume is increasing slowly the entire seed is getting swell so that is osmosis is happening. So when it will reach a particular

stage so that it cannot withstand or it cannot take up take more water then it will burst. So and this germination of seeds actually essentially is happening due to the intake of water inside the sun due to osmosis.

So, this causes drawing of water from the soil to the root system of the plants and can bust up on by immersing them in a solution which is having much lower osmotic pressure. As far as membrane processing is concerned its major significance lies in the fact that external pressure must be applied for significant permeate flux must be higher than osmotic pressure of the solution. The basic relationship between applied pressure you can assume a pressure applied by a pump osmotic pressure and the flow of solvent through the membrane is like many transport processes express in terms of flux and the driving force is resistances.

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For an ideal semi-permeable membrane:
$J = A(P_T - \pi_F)$
where, J is the flux, A is the membrane permeability coefficient, $P_T$ is transmembrane pressure,
$\pi_{k}$ is the osmotic pressure of feed solution.
• Thus, there has to be a positive driving force for flux ( <i>i.e.</i> $P_T$ should be always greater than $\pi_F$ ).
· Even relatively small concentrations of dissolved solutes can develop fairly large osmotic
pressure.
A concentration difference of 0.1 M across a membrane can result in osmotic pressure of about
2.5 bar (~37 <i>psi</i> ).
Image: Second state of the se

So for an ideal semi permeable membrane we can write j = A into PT - pi F. Where J is the flux A is the membrane permeability coefficient PT is the transmembrane pressure and pi F is the osmotic pressure of the feed solution. Since F is been given in the superscript. So it denotes that the osmotic pressure is for the feed solution that there is to be a positive driving force for flux that is PT should be always greater than the pi F.

Otherwise there will be no flux. Even relatively small concentrations of dissolved solutes can develop fairly large osmotic pressures. So a concentration difference of 0.1 molar across a

membrane can result in osmotic pressure of about 2.5 bar So this we have seen approximately 30 pipe psi.

# (Refer Slide Time: 30:42)

2	58.50	NaCl
1	342	Lactose
1	25000	Casein
1		

We have seen in one of the tables. So the table is again showing some example of osmotic pressure calculations using van't Hoff equation. So the component is let us see sodium chloride its molecular weight per 58.5 number of irons 2 osmotic pressure is 125 lactose number of irons 1 osmotic pressure is 10 casein number of irons 1 osmotic pressure is still low. So you can see the effect of molecular weight and osmotic pressure also.

# (Refer Slide Time: 31:11)

The osmotic pressure data for macromolecules (or colloidal solutes) are few, especially as a function of concentration.
This is unfortunate since at sufficiently high concentration, the osmotic pressure becomes significant (especially at membrane surface due to polarization phenomenon).
Osmotic pressure data obtained from reverse osmosis experiment must be used with caution, since it is frequently obtained by the extrapolation of flux data to zero flux.
If van't Hoff is used for calculation of osmotic pressure, it should be remembered that it assumes that osmotic pressure will increase in linear fashion with solute concentration.

The osmotic pressure data for macromolecules or colloidal solutes are few especially as a function of concentration. So this is unfortunate since at sufficiently high concentration the osmotic pressure becomes significant or especially at membrane surface due to polarization phenomenon. So actually what is happening when the solution getting deposited whether it is s salt or any other salute on the surface of the membrane thereby developing this concentration polarization layer?

So a sufficiently high concentration the osmotic pressure becomes significant. So osmotic pressure data obtained from reverse osmosis experiment must be used with caution, since it is frequently obtained by the extrapolation of flux data to 0 flux. So the van't Hoff question is used for calculation of osmotic pressure. It should be remembered that it assumes that osmotic pressure will increase in linear fashion with solute concentration. So the data from van't Hoff equation has to be used with causes.

(Refer Slide Time: 32:07)

Compounds	Concentration	Osmotic pressure (psi)
Milk	9% solid non-fat	100
Whey	6% total solids	100
Orange juice	11% total solids	230
Apple juice	15% total solids	300
Grape juice	16% total solids	300
Coffee extract	28% total solids	500
Lactose	5% w/v	55
Sodium chloride	1% w/v	125
Lactic acid	1% w/v	80
Sweet potato waste water	22% total solids	870

So this table gives the osmotic pressure of various compounds at 25 degrees centigrade. So you can see when the solid concentration actually is increasing. So you have osmotic pressure will also increase and as we discussed osmotic pressure is completely dependent upon near the concentration it has nothing to do with the solute size and sip.

(Refer Slide Time: 32:31)

#### Isotonic solution

- · Solutions having same osmotic pressure are known as isotonic solutions.
- An isotonic cellular environment occurs when an equal solute concentration occurs exists inside and outside of cell.
- Water molecule flows in and out at an equal rate by osmosis, causing the cell size to stay the same. As a result, it will not gain or lose any solute.
- · Plant cell in an isotonic environment is flaceid, and they will wither.
- The equilibrium of water movement is unable to provide plant cells with internal pressure for structural support, and therefore plants prefers hypotonic environment.
- In this situation, the concentration of solute inside plant cell is higher than outside, and the plant cell uses active transport to transport solutes in.
- This ensures that the concentration of water will be higher outside plant cell than inside.

So what is an isotonic solution? This stomps many times we will hear when you are doing something with osmosis. So solutions having same osmotic pressures are known as isotonic solutions. So an isotonic cellular environment occurs when an equal solid concentration occurs exists inside and outside of the cell. So water molecules flows in and out and then equal read by osmosis causing the cell size to stay the same as a result it will not gain or lose any solute. So plant cell in an isotonic environment is flaccid and they will wither.

The equilibrium of water movement is unable to provide plant cells with internal pressure for structural support and therefore plants prefers hypotonic environment. In this situation the concentration of solute inside plant cell is higher than outside and the plant cell uses active transport to transport solute in. This ensures that the concentration of water will be higher outside the plants cell then inside.

# (Refer Slide Time: 33:33)

- There are two types of osmosis:
  - Direct osmosis

DO uses low pressure. The solvent passes through the membrane driven by the difference in solute concentrations on the two sides. Equilibrium is reached when sufficient water has moved to equalize the solute concentration on both sides of the membrane.

<u>Reverse osmosis</u>

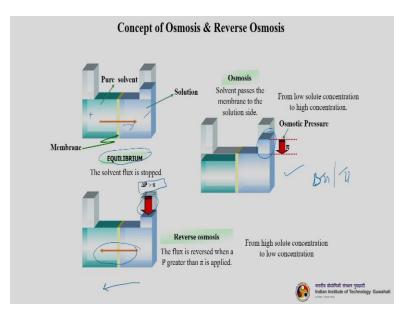
RO uses a high-pressure which is larger than OP on the high concentration side. So, the carrier is preferentially permeated, while the retentate contains the rejected solute (contaminant). Thus, the membrane divides the water from the contaminants. The main aim is to purify water and not dilute the contaminants.

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So there are 2 different types of osmosis is there one is the direct osmosis and other is the reverse osmosis. So direct osmosis uses low pressure and the solvent passes through the membrane driven by the difference in solute concentrations on the 2 sides. Equilibrium is reached when sufficient water has moved to equalize the solute concentration on both sides of the membrane. Now reverse osmosis uses high pressure which is larger than the osmotic pressure on the high concentration phase or side.

So the carrier is preferentially permeated by the retentate contains the rejected solute or that they are basically the contaminant thus the membrane divides the water from the contaminants the main aim is to purify water or but not to dilute the contaminants.

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So let us have a look in this particular slide here again I am trying to explain you the concept of osmosis and reverse osmosis you can see the first one here this one this is an equal this particular figure it is showing that the system is in equilibrium. So one said there is a pure solvent and they say there is a solution this is a solution this is your pure solvent. So when the system is equilibrium, there will be no flow and the system is not any equilibrium.

The flow of dilute solvent or water molecule from pure to the concentrator sides all takes place in this particular direction. Now when osmosis will happen this is what I was just doing explaining that solvent passes to the membrane to the solution side when there is no equilibrium then as a result the concentrated side the volume will increase basically and will digest something in a rise in the (())(35:19) sides and that is being expressed as a pi which is given by the osmotic pressure. So from low solute concentration to the high solute concentration.

Now please remember that what will happen or how we will achieve reverse osmosis so reverse osmosis will be achieved when delta p will be much higher than that delta pi. So we will apply a pressure in such a way that or will apply the pressure which is much higher than the osmotic pressure we know from here or from here we can calculate what is the osmotic pressure difference delta Pi so or pie let us or p.

And we know how much pressure we need to apply which is more than this pi. So that we will achieve that it was direction of the flow. So when we apply hard pressure than that of the pi the flux is reversed when P is greater than pi. So your flow takes place in this direction from high solute concentration to low concentration. Please remember only water is passing because the membrane is semi permeable no solute is passing through the membrane.

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#### **Concept of Reverse Osmosis**

- As illustrated in figure osmosis is a natural phenomenon where water passes through a membrane from a side with lower solute concentration to a higher solute concentration until the osmotic equilibrium is reached.
- To reverse the water flow, a mechanical pressure is applied, providing the pressure difference greater than the osmotic pressure difference; as a result, separation of water from a solution becomes possible. This phenomenon is called *reverse osmosis*.



As illustrated in the earliest figure you know that osmosis is a natural phenomenon when water passes through a membrane from a side of lower concentration to higher concentration whereas the reverse osmosis is not a natural phenomenon to achieve reverse osmosis we need to apply mechanical pressure which is much higher than that of the osmotic pressure.

## (Refer Slide Time: 36:44)

#### **Concept of Reverse Osmosis**

- To reverse the natural process of osmosis, it is required to overcome the osmotic pressure equilibrium across the membrane because flow is naturally from dilute to concentrated.
- If we want more pure water, we must increase the salt content in the cell (i.e. the concentrated side of membrane).
- To obtain this we need to increase the pressure on the salty side of the membrane and force the water across.
- The amount of pressure is determined by the salt concentration increases requiring even greater pressure to get more pure water.
- By exerting a hydraulic pressure greater than the sum of the osmotic pressure difference and the pressure loss of diffusion through the membrane, we can cause water to diffuse in the opposite direction.

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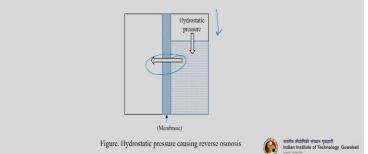
If we want more pure water so we must increase the salt content in the cell. So this is one way to achieve the reverse osmosis easily also that (())(36:53) concentrated side of the membrane is concentration further increases. So to obtain this we need to increase the pressure on the salty side of the membrane and hence the and force the water across. So that means we are creating a more water better grad tainted chemical potential.

The amount of pressure is determined by salt concentration increase requiring even greater pressure to get more pure water by exerting a hydraulic pressure greater than the sum of the osmotic pressure difference and the pressure loss of diffusion through the membrane we can cause water to diffuse in the opposite direction.

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#### **Concept of Reverse Osmosis**

- The greater the pressure applied, the more rapid will be diffusion. It follows that if other variables are kept constant, the water flow-rate becomes proportional to the net pressure.
- Using reverse osmosis, it is possible to concentrate various solutes, either dissolved or dispersed, in a solution.
- It has the separation range of 0.0001 0.001 µm particle size.



So the greater the pressure applied the more rapid will be diffusion. So it follows that if other variables are kept constant water flow rate becomes proportional to the net pressure that means the essentially what it means it means that whatever pressure you are applying from here that is directly related to whatever the florid that is happening here. So using reverse osmosis, it is possible to concentrate various solutes either dissolved or dispersed in a solution. So it is a separation range of 0.0001 to 0.001 micro particle size very small since it is basically dealing with the irons.

# (Refer Slide Time: 38:01)

#### Advantages of reverse osmosis

- Reverse osmosis, is the most important process of desalination of brackish (1000 5000 ppm salt) or sca water (about 35,000 ppm).
- · Over conventional separation processes, reverse osmosis has following advantages:
  - Since, RO is a pressure driven process, no energy intensive phase change or potentially expensive solvents or absorbents are needed for RO separation.
  - It is inherently simpler to design and operate than many traditional separation processes.
  - iii. Simultaneously, separation and concentration of both inorganic and organic compounds are possible using RO process.
  - iv. It can be combined with conventional separation processes such as distillation to provide a hybrid process.

Reverse osmosis is the most important process of desalination of brackish water in which about 30 pipe brackish water the concentration is usually 1000 to 5000 ppm where and sea water are

also in sea water is about 35000 ppm very high. So over conventional separation processes RO has the following advantages RO is a present even process or no energy intensive phase change or potentially expensive solid solvents or absorbents are needed.

It is inherently simpler to design and operate than many traditional separation processes. Simultaneously separation and concentration of both inorganic and organic compounds are possible using the RO process. It can be combined with conventional separatism processes such as distillation to make a hybrid separation process.

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#### Concept of Reverse Osmosis

- In summary, the major resistances to overcome in reverse osmosis are the resistance of the membrane, osmotic pressure of the solutes, and possibly mass transfer resistance in the boundary layer and to a lesser extent to the membrane resistance itself, depending on the feed properties, and the operating conditions.
- Under certain conditions and with certain solutes, the osmotic pressure may become the limiting factor in ultrafiltration also.
- Thus, the operating strategy to maximise the flux depends on the mechanism of the limiting flux.

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In summary the major resistance to overcome in reverse osmosis as the resistance of the membrane osmotic pressure of the solute and possibly mass transfer resistance in the boundary layer and to a lesser extent to the membrane resistance itself depending on the feed properties and the operating conditions under certain conditions and with certain solutes the osmotic pressure may become the limiting factor in ultrafiltration also. Now thus operating strategy to maximize the flux depends on the mechanism of the limiting flux. So let us try to solve very to small numericals on osmosis. And the question goes something like this.

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#### **Practice Problems**

<u>Question</u>: Calculate the osmotic pressure of the solution containing 0.10 g mol NaCl / 1000 g H<sub>2</sub>O at 25 °C. Given that the density of water at 25 °C is 997  $kg/m^3$ .

$$Naci = 9 \cdot 2 \cdot 10^{17}$$

$$N = 2 \times 0.84 \times 10^{-3} = 1.68 \times 10^{-3}$$

$$Volume old pure colvent, Vm = \frac{1}{997} m^{3}$$

$$TI = \frac{M}{V_{m}} RT = \frac{1.68 \times 10^{-3} \times 82.057 \times 10^{-3} \times 298.15}{\frac{1}{997}}$$

$$T = 40.975 \text{ abus}$$

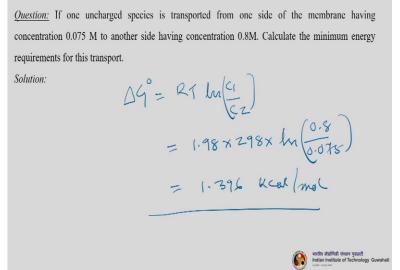
$$RT = 40.975 \text{ abus}$$

So, calculate the osmotic pressure of the solution containing 0.01gram mols sodium chloride per 1000 gram of water at 25 degrees centigrade and we have been given the density of water at 25 degrees centigrade is 997 kg per meter cube. So let us try to solve this since soul NaCL when NaCL will dissociate no NSL dissociates it gives 2 irons. Sodium plus and chlorine minus. Now n = 2 into 0.84 into 10 power of - 3 which is we can write 1.68 into 10 power of - 3.

So the volume of pure water pure solvent which is required to calculate so V m = 1 divided by you know this 997 so it is in meter cube. So the osmotic pressure becomes pi = n / V m into RT so that is 1.68 into 10 power of – 3 into 82.057 into 10 power of – 3 into 298.15 divided by 1 / 997. So pi becomes 40.978 atmospheres we will see more numericals on later on in one of our classes when we wind up discussing RO. So this is just a small very small example how do you calculate actually osmotic pressure so another very small one.

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# Practice Problems



If one uncharged species is transported from one side of the membrane having a concentration of 0.075 mol to another side have been concentration of 0.08m mol than calculate the minimum energy requirement for this transport. So that means they are asking us to calculate the delta G naught which is RT ln C 1 / C 2. So you can write 1.98 into 298 into ln 0.8 divided by 0.075. So this gives me 1.396 kilo calorie bar mol. So this is how we calculate the free energy. So these are the 2 small examples that we discussed today. Obviously as I told you that we will try to solve more numericals in our subsequent lectures.

# (Refer Slide Time: 42:47)

## Text/References

- M. H. Mulder, Basic Principles of Membrane Technology, Springer, 2004
- B. K. Dutta, Mass Transfer and Separation Processes, PHI, 2007.
- K. Nath, Membrane Separation Processes, PHI, 2008.
- M. Cheryan, Ultrafiltration & Microfiltration Handbook, Technomic, 1998.
- · Richard W. Baker, Membrane Technology and Applications, Wiley, 2012.



Now please refer to the textbook Mulder as I am telling you Mulder we have adapted as a text for this particular course as well as Professor Nath books also it is a very nice book you can please refer to this book also. So and there are other books as given by B.K. Dutta and M. Cheryn and Richard Baker. So if you do not have access to all other soils such as that please try to have access to at least Mulder and KNR book.

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Module	Module name	Lecture	Title of lecture
06	Reverse osmosis, Nano-filtration, and Ultrafiltration	15	Pressure requirement, high pressure and low pressure RO, membrane materials, modules, models for RO transport
	2		mmpor

So thank you very much. And the next class we will discuss about the pressure requirement, high pressure and low pressure. RO membrane and materials models and models for RO transport. So thank you very much. In case you have any query to fill, please write to me at <u>kmohanty@iitg.ac.in</u>. Thank you.