Chemical Engineering Thermodynamics
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Lecture 58: Examples of boiling point elevation

Welcome back! In the last class, lecture was basically on boiling point elevation and freezing point depression that is the effect of a solute on the properties related to the boiling and freezing points. In addition, of course, we are going to talk about other coagulative properties that is osmotic pressure, but currently we looked into two aspect of that. So, we can start with today's lecture with an example illustrating this concept of you know boiling point evolution, particularly let us say for sea or water.

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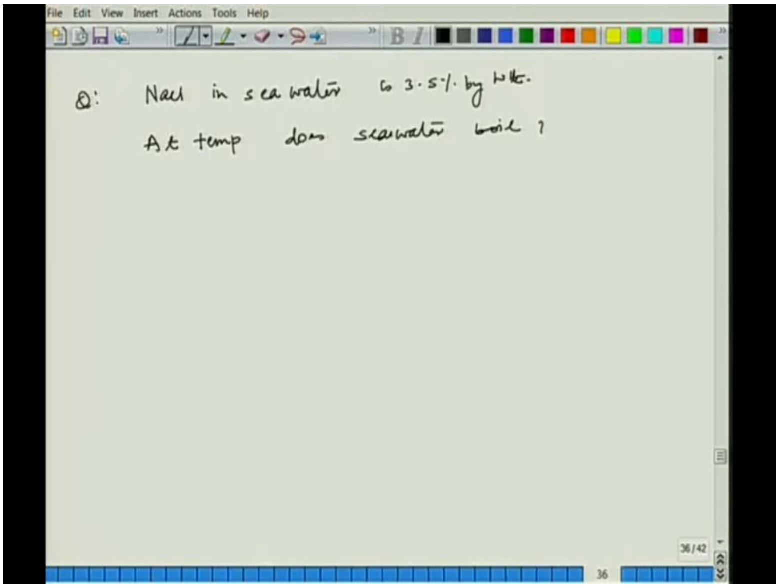

Q: NaCl in sea water is 3.5% by wt.

At temp does seawater boil ?

Okay. So, the simple question could be something like if you consider let us say NaCl in sea water is let us say 3.5 percent by weight, okay. So, at what temperature does sea water boil? So here we have a simple question related to this boiling point elevation.

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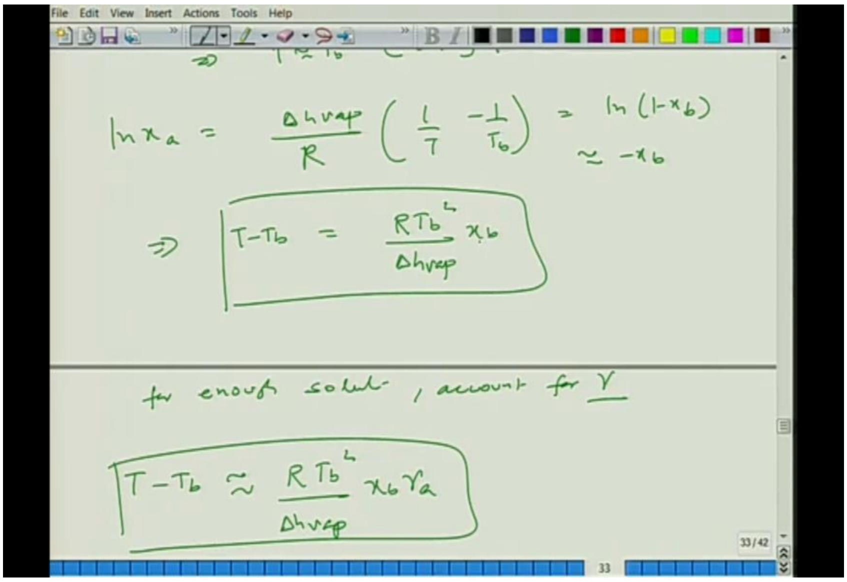

$\Rightarrow T \approx T_b$

$$\ln x_a = \frac{\Delta h_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right) = \ln(1-x_b) \simeq -x_b$$

$$\Rightarrow \boxed{T - T_b = \frac{R T_b^2}{\Delta h_{vap}} x_b}$$

for enough solute, account for $\underline{\gamma}$

$$\boxed{T - T_b \simeq \frac{R T_b^2}{\Delta h_{vap}} x_b \gamma_a}$$

$$T - T_b = \frac{RT_b^2}{\Delta h_{vap}} x_b \gamma_a$$

So, if you can see this expression here okay, it talks about a simple like this right like this your expression related to the shift in the boiling point and that depends on your solute concentration. So, let us look at how do we calculate x b okay and we are also asking we need also this particular expression or value of vaporisation the delta h vaporisation as well as the TB okay which is the boiling point for the pure substance okay.

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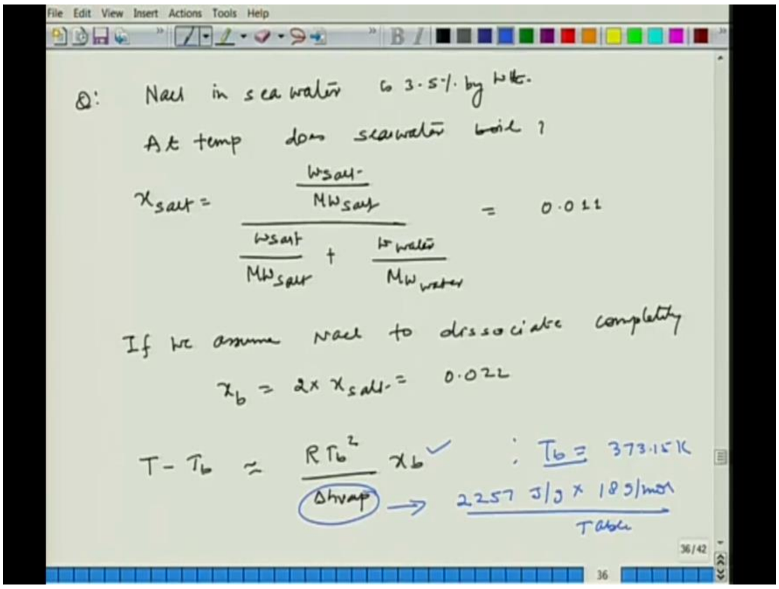

Q: NaCl in sea water is 3.5% by wt.

At temp does seawater boil ?

$$x_{salt} = \frac{\frac{w_{salt}}{MW_{salt}}}{\frac{w_{salt}}{MW_{salt}} + \frac{w_{water}}{Mw_{water}}} = 0.011$$

If we assume NaCl to dissociate completely

$$x_b = 2\times x_{salt} = 0.022$$

$$T - T_b \simeq \frac{RT_b^2}{\boxed{\Delta h_{vap}}} x_b \checkmark \quad ; \underline{T_b = 373.15\,K}$$

$$\Delta h_{vap} \rightarrow \underset{\text{Table}}{\underline{2257\ J/g \times 18\ g/mol}}$$

$$x_{salt} = \frac{\frac{w_{salt}}{Mw_{salt}}}{\frac{w_{salt}}{Mw_{salt}} + \frac{w_{water}}{Mw_{water}}} = 0.011$$

$$If\ we\ assume\ NaCl\ to\ dissociate\ completely$$

$$x_b = 2 \times x_{salt} = 0.022$$

$$T - T_b = \frac{RT_b^2}{\Delta h_{vap}} x_b = 0.63\ \text{K}$$

So, in this case salt, of course, we are talking about so salt is could be the weight of salt, okay, so what we need is the composition or the mole fraction of it and this would be molecular weight of the salt. And then weight of the salt by M W of the salt plus that of the water divided by M W of water. So, if you do this, of course, this is the 0.35, 0.035 as the weight and then the molecular weight is that of Na and Cl.

So, if you plug in all this information available to you, it is going to be 0.011. Now, the important thing is that the salt here will dissociate in water because of the dielectric constants of the water and considering that you will have Na plus and Cl minus. So, if we assume NaCl to dissociate completely then X of b which is there in expression is two times that of the x of salt okay which is going to be 0.022.

So that will be the effective solute present as the mole fractions are concerned. So now we need to find out the shift or in the boiling point or enhancement in the boiling point. In this case elevation so this we have approximated to T b square by delta H vapour X of b. Okay, so now X of b is we know, the T b here original T b at the atmospheric pressure because it is in sea water.

So, essentially you are talking about just under atmospheric pressure condition that will be your and since we are saying boiling point which is usually refers to that when it comes to normal boiling point. So, T b at atmospheric pressure would be your 373.15 kelvin. What about delta h v? So, delta h v again at this condition would be 2257 joules per gram multiplied by 18 gram per mole. So, this comes from the table okay this comes from the same table at 373.15 kelvin.

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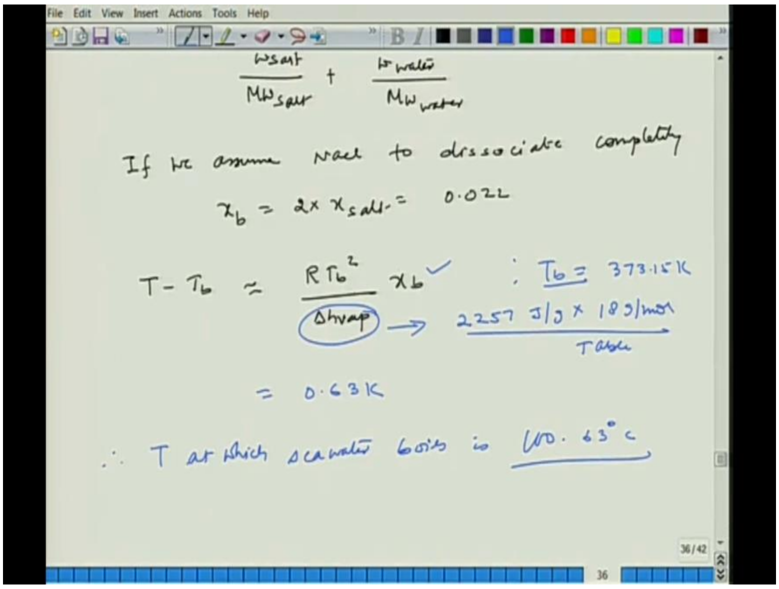

$$\frac{w_{salt}}{MW_{salt}} + \frac{w_{water}}{MW_{water}}$$

If we assume NaCl to dissociate completely

$$x_b = 2 \times x_{salt} = 0.022$$

$$T - T_b \simeq \frac{RT_b^2}{\boxed{\Delta h_{vap}}} x_b \checkmark \quad ; \; \underline{T_b =} \; 373.15\,K$$

$$\Delta h_{vap} \rightarrow \underset{Table}{\underline{2257\ J/g \times 18\ g/mol}}$$

$$= 0.63\,K$$

$\therefore$ T at which seawater boils is $\underline{100.63^\circ C}$

Okay so given this we can find out the change and that change comes out to be 0.63 kelvin. Thus, the temperature at which sea water boils is 100.63 degree Celsius. So, this is a very simple illustration of how one would be using these expressions which we have evaluated for the case of boiling point elevation or freezing point depression to find out necessary information.

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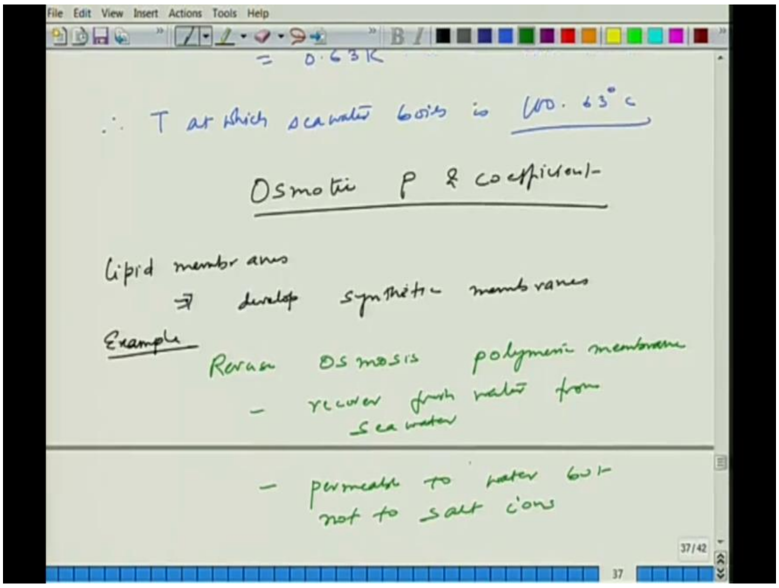

= 0.63 K

∴ T at which seawater boils is 100.63°C

Osmotic P & coefficient

lipid membranes
⇒ develop synthetic membranes

Example
Reverse osmosis polymeric membrane
- recover fresh water from sea water
- permeable to water but not to salt ions

So, now we can actually move on to the specific case of coagulative property and that is related to the osmotic pressure. So, we move on to the last aspect of this, okay. This is an extremely important aspect because life particularly depends on the lipid membrane which we have in our body and essentially it allows only a certain species to move or transport, you know, and others it rejects. And that is essentially important aspect for our cells, it separates interiors of the cells from the environment and that is some specific kind of a motivation which has led to synthetic membrane.

So, lipid membrane properties have motivated to develop a synthetic membrane which allows only specific species to move. Its example could be, the example could be reverse osmosis polymeric membrane which is often used to recover fresh water from sea water. So, in such a case when its reverse osmosis polymeric membrane it basically is permeable to water but not to salt, salt ions.

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So, let us look at this concept of this by analysing the thermodynamic basis of such a system. So, let us do a bit of thermodynamic analysis of such membranes which allows only specific components to pass. So, in this case what we are going to do is we will consider two compartments. So, let me just draw that okay, so then let us consider two compartments, so which is maintained at certain pressure and what we have is this semi permeable membrane.

So, essentially you have water, okay, so let me use the same colour water. So, here is also water, but in addition to that you have these salts or solutes which are not permeable to membrane okay. So, I am going to call this compartment as first compartment this another compartment is second compartment. So, we will worry about the pressure acting on this but let us first understand the conditions of the equilibrium which we know that the temperature has to be equal.

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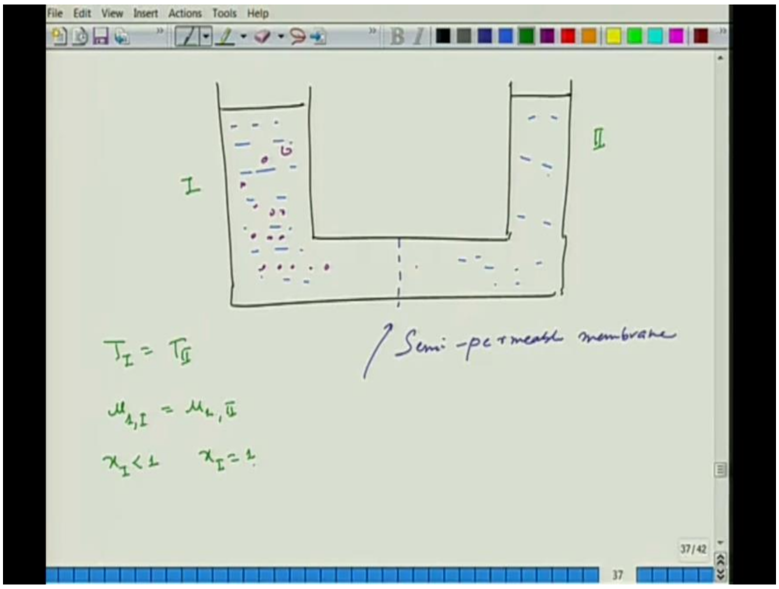

$$T_I = T_{II}$$

$$\mu_{1,I} = \mu_{1,II}$$

$$x_I < 1 \quad x_I = 1$$

$$P_I > P_{II}$$

So, the conditions are the temperatures of in the first compartment must be equal to the temperature of the second compartment. And there are two species one is water and the other one is solute so water we can say is one and then we are saying that you know the chemical potential of water in one compartment 1 is should be same as the chemical potential of water in the second compartment.

Or in general the solvent, so one could be solvent and the solute is two. But since there is no solute present in the second compartment there is no condition for mu 2 because species 2 is not allowed to move in. Now, at equilibrium you have this condition but you also note that if I just look at the composition of this the mole fraction of water or solvent then essentially following conditions occur, that x of 1.

If x stands for that of the solvent then this is going to be less than 1 and this in this case this is going to be 1. Now, when you have these two different conditions then how come this is unequal. So, this must mean that given that the temperature is same the pressure cannot be the same it is clearly the pressure has to be different.

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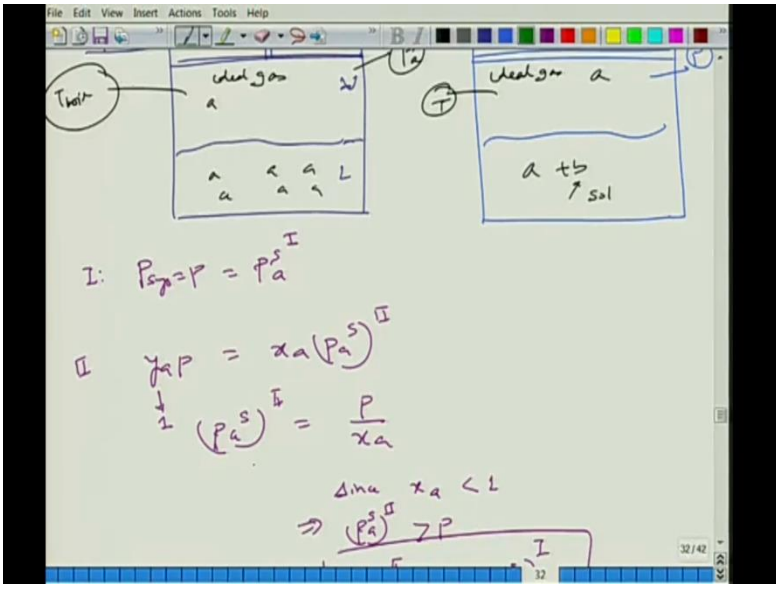

$$I. P_{sys} = P = P_a^s$$

$$II. y_a P = x_a (P_a^s)^{II}$$

$$(P_a^s)^I = \frac{P}{x_a} \quad since\ x_a < 1\ \ or,\ \ (P_a^S)^{II} > P$$

Now, this is where we need to go back and see what we used earlier these concepts of change in the composition would lead to the conditions change in the conditions such that the pressure okay in the compartment let us say in this case where we added some solute need to be more than that corresponding to that in the pure case.

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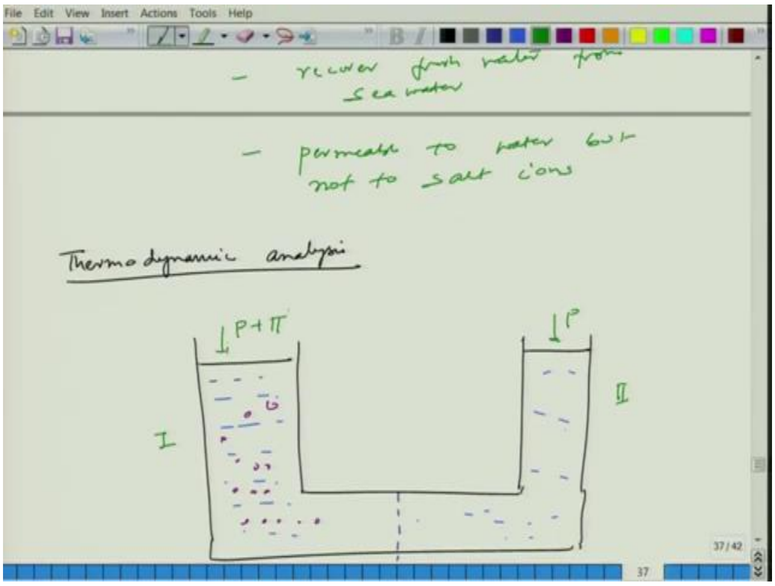
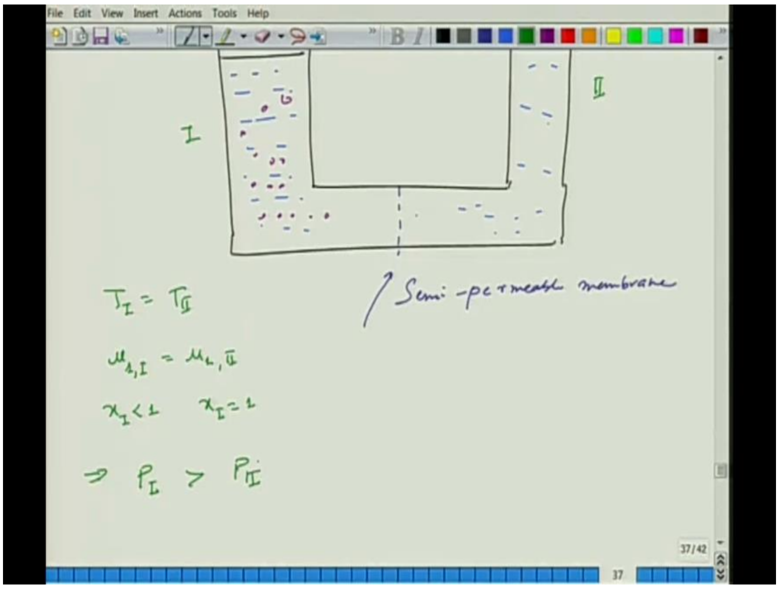


– recover fresh water from sea water

– permeable to water but not to salt ions

Thermodynamic analysis



$T_I = T_{II}$

$\mu_{1,I} = \mu_{1,II}$

$x_1 < 1 \quad x_{I} = 1$

$\Rightarrow P_I > P_{II}$

So, if you use that understanding of the past which we have done this exercise. For that case we have used a vapour liquid but the same thing can be used here, that the pressure need to be more in the compartment where you have composition less than 1 and this is necessary for maintaining such an equilibrium okay.

This is also true that your potential would be lower at a lower pressure. So, given this it tells you the pressure in compartment 1 should be greater than pressure in compartment 1. And if that is case then, let us say if the pressure is P here then this pressure should be P plus some additional pressure which I am saying pi in order to maintain the equilibrium okay.

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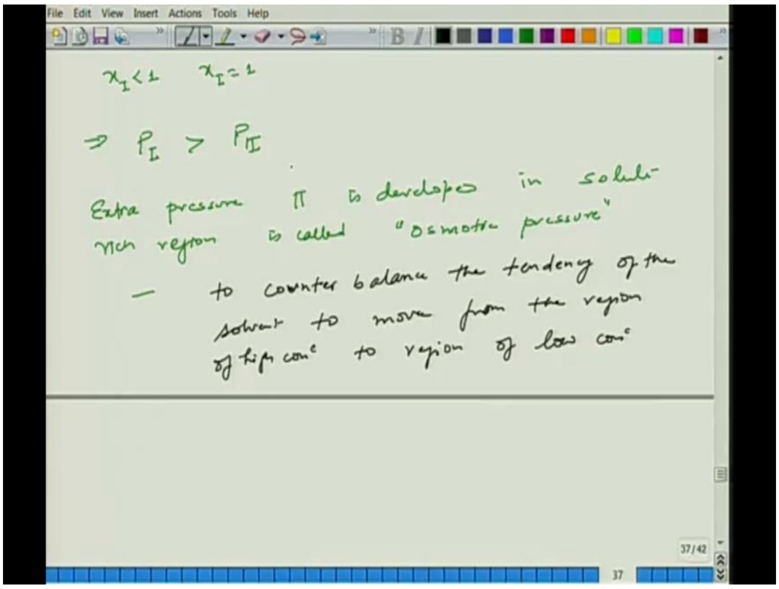

$x_I < 1 \quad x_I = 1$

$\Rightarrow P_I > P_{II}$

Extra pressure π is developed in solute rich region is called "Osmotic pressure"

– to counter balance the tendency of the solvent to move from the region of high conc to region of low conc

So, this is extra pressure which pi is developed in the solute rich region for such a system is called Osmotic Pressure. So this is necessary in some sense because this will maintain the equilibrium oaky. So this pi is the required to this extra pressure is required to counter balance the tendency of the solvent which is at a higher concentration in the right compartment transport to the left compartment, tendency of the solvent to move from the region of high concentration to region of low concentration, okay.

So it clearly tells you that since this x is equal to 1 so it will try to move here but then if you want an equilibrium in such a case you need to put extra pressure here in this particular compartment so that you can counter balance the movement of the solvent in the in this direction okay. So, that is how developed this kind of membrane. Now, in such a case you can also apply thermodynamic understanding to come up with a relation of fugacity to compositions of the solute in this case as well as the non-ideality of the mixtures. So, how you are going to go about it?

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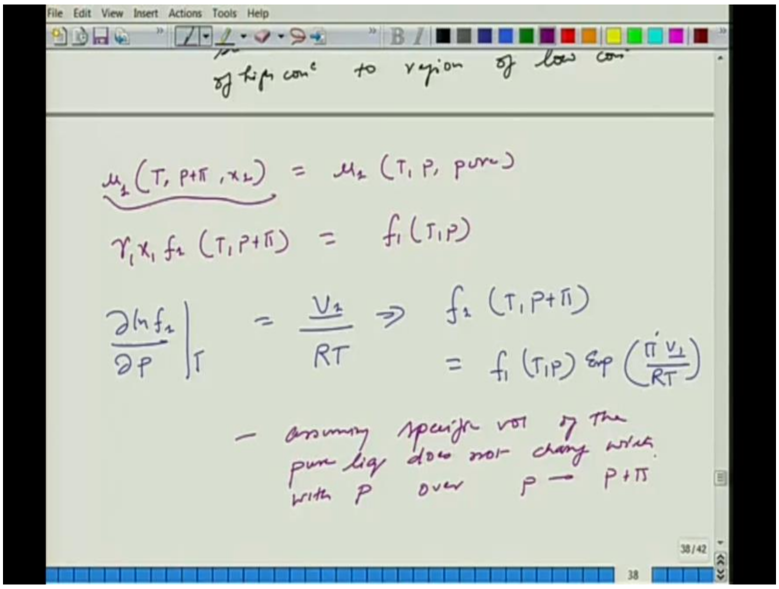

of high conc to region of low conc

$\underbrace{\mu_1(T, P+\pi, x_1)} = \mu_1(T, P, \text{pure})$

$\gamma_1 x_1 f_1(T, P+\pi) = f_1(T, P)$

$\left.\frac{\partial \ln f_1}{\partial P}\right|_T = \frac{\underline{V}_1}{RT} \Rightarrow f_1(T, P+\pi) = f_1(T, P)\,\text{Exp}\left(\frac{\pi \underline{V}_1}{RT}\right)$

– assuming specific vol of the pure liq does not change with with P over P → P+π

$$\mu_1(T, P+\pi, x_1) = \mu_1(T, P, pure)$$

$$\gamma_1 x_1 f_1(T, P+\pi) = f_1(T, P)$$

$$\frac{\partial \ln f_1}{\partial P}|_T = \frac{\underline{V}_1}{RT} \qquad or, \qquad f_1(T, P+\pi) = f_1(T, P)\exp(\pi \underline{V}_1 / RT)$$

$$\frac{\pi \underline{V}_1}{RT} = -\ln(\gamma_1 x_1)$$

$$\pi = -\frac{RT}{\underline{V}_1}\ln(\gamma_1 x_1)$$

So, we can start with the same concept here because our major condition of equilibrium is related to the chemical potential. So, now, I can write this chemical potential little bit more clearly so I am still talking about the solvent case here okay and here of course is T and the pressure here is different, okay. So this pressure and this composition of that so pressure I am going to expand it, this pressure is nothing but P plus pi this is going to be the same as mu 1 T P and this is pure.

Now, this, I can write this thing as we have done in an earlier case as gamma 1 x 1 f 1 and again this is P plus pi. So, that is the reference case we have particularly the fugacity at that particular condition. So this is the Lewis Randall reference we are considering and this of course I can write this as T P. Alright now if we make use of the relation here of fugacity with pressure dependency, I can write the earlier expression which we have got. We know this that d log of f with respect to P is nothing but related to molar volume divided by RT.

So this could be written now for the case of water. And if that is the case I can write this as f 1 at T plus P plus pi, this would be your f of 1, T of p because we are adding additional pressure and this additional pressure come as a part of pi V 1 bar underscore RT okay. So, this pi nothing but delta P, so this is more like a pointing correction okay. So, now we are assuming here of course we have integrated but we assumed that specific volume of the pure liquid does not change with P over P to P plus pi so that is the range we are.

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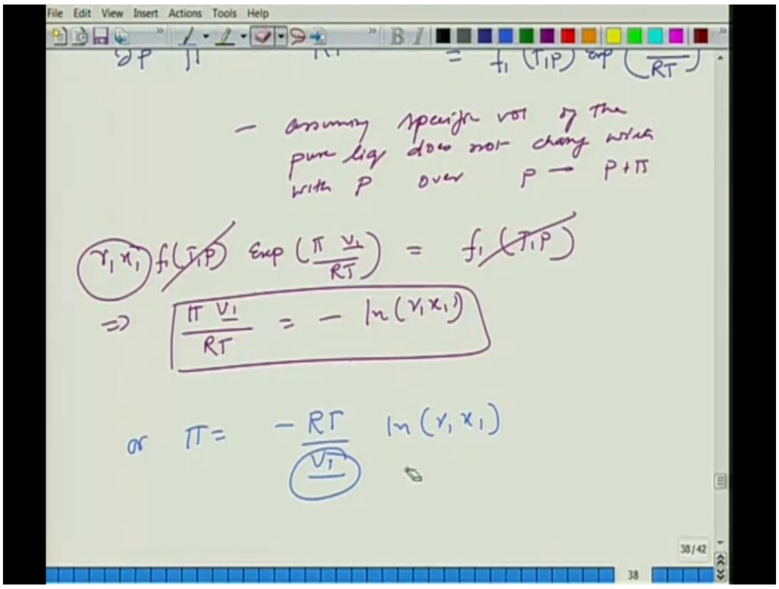

$= f_1(T,P)\,\exp\left(\frac{\quad}{RT}\right)$

– assuming specific vol of the pure liq does not change with with P over P → P+π

$$\boxed{\gamma_1 x_1}\,\cancel{f(T,P)}\;\mathrm{Exp}\left(\frac{\pi \bar{V}_1}{RT}\right) = f_1\cancel{(T,P)}$$

$$\Rightarrow \boxed{\frac{\pi \bar{V}_1}{RT} = -\ln(\gamma_1 x_1)}$$

$$\text{or}\quad \pi = -\frac{RT}{\boxed{\bar{V}_1}}\ln(\gamma_1 x_1)$$

Now, given this information we can plug in back here, so now I have gamma 1 x 1 f 1 T P and this exponential term pi of V 1 bar by RT and this must be equal to F 1 T P, so this can cancel now and I have is pi V1 bar R T is minus of because I have a log here and if I take log then this will be in the denominator and hence, I am going to get negative log of gamma x 1. So, this is something which I have now I can further simplify to get my relation of pi or pi is minus R T by V1 bar ln gamma 1 x 1 okay. This, I can also write this like this but usually we have this for pure case so we can get rid of this now.

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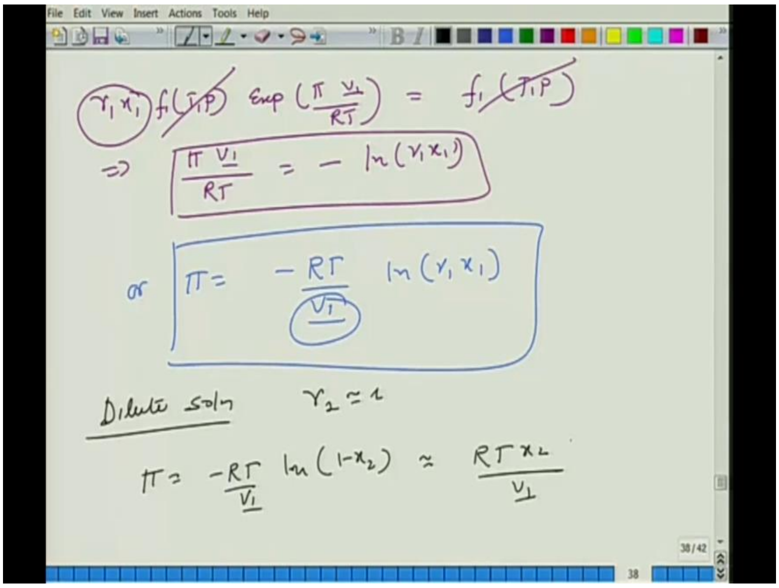

$$\boxed{\gamma_1 x_1} \cancel{f_1(T,P)} \operatorname{Exp}\left(\frac{\pi \underline{V}_1}{RT}\right) = \cancel{f_1(T,P)}$$

$$\Rightarrow \boxed{\frac{\pi \underline{V}_1}{RT} = -\ln(\gamma_1 x_1)}$$

$$\text{or} \quad \boxed{\pi = -\frac{RT}{\underline{V}_1} \ln(\gamma_1 x_1)}$$

Dilute soln $\gamma_2 \simeq 1$

$$\pi = -\frac{RT}{\underline{V}_1} \ln(1-x_2) \approx \frac{RT x_2}{\underline{V}_1}$$

So, let us consider the case for the dilute solution, so we have this beautiful relation which relates the osmotic pressure with composition and activity coefficient. So, now, I can consider a specific cases of let us say dilute solution which essentially means I can approximate this to 1 and then there is minus RT V 1, of course, there is x 1 can be written as log of 1 minus x 2 and now since x 2 is extremely small we can use a tailor expansion. And this expansion can be written as R T x 2 by V 1 bar and this further can be simplified as follows.

$$Dilute\ soln.\ \gamma_1 \approx 1$$

$$\pi = -\frac{RT}{\underline{V}_1} \ln(1-x_2) = \frac{RTx_2}{\underline{V}_1}$$

$$\pi \underline{V}_1 N = RTN_2$$

$$\pi = \frac{RTN_2}{V} = RTC_2$$

$$MW_2 = \frac{RTC_2}{\pi}$$

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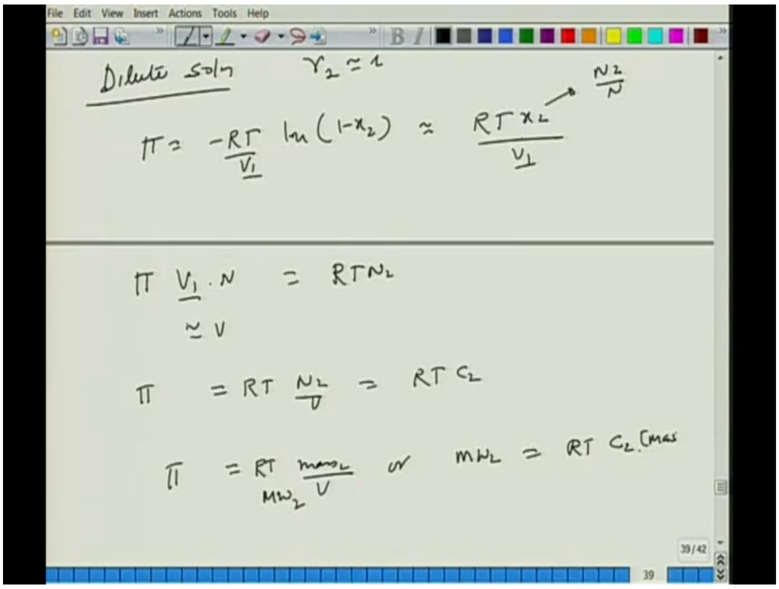


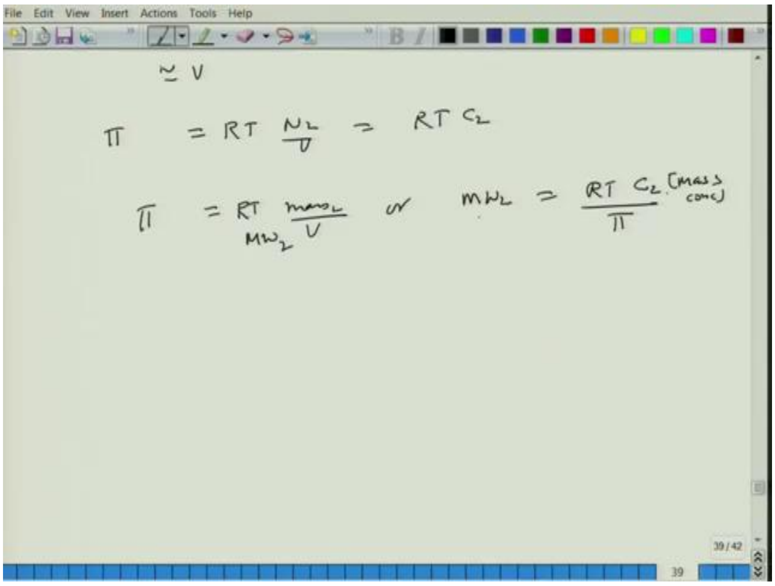
Dilute soln $\quad \gamma_2 \simeq 1$

$$\pi = -\frac{RT}{\bar{V}_1}\ln(1-x_2) \simeq \frac{RT\overset{\frac{N_2}{N}}{x_2}}{\bar{V}_1}$$

$$\pi \underbrace{\bar{V}_1 \cdot N}_{\simeq V} = RTN_2$$

$$\pi = RT\frac{N_2}{V} = RT\,C_2$$

$$\pi = RT\frac{mass_2}{MW_2\,V} \text{ or } MW_2 = RT\,C_2\text{(mas}$$



$$\simeq V$$

$$\pi = RT\frac{N_2}{V} = RT\,C_2$$

$$\pi = RT\frac{mass_2}{MW_2\,V} \text{ or } MW_2 = \frac{RT\,C_2\text{(mass conc)}}{\pi}$$

So, I can write this as N 2 by N, number of moles by N and this N times V 1 can be written as V 1 bar times N. This I can approximate by V because of the dilute part and this R T N 2 it can come okay. And this expression also now can be written as R T N 2 by V this is nothing but R T C 2 concentration. So, this is what we have now so pi can be directly related to the concentration of the solute in the case of direct solutions.

I can also write this you know this is a basically, a concentration which essentially means number of moles divided by V. Now you can also rewrite this expression in two if you want to find out let us say molecular weight then I can instead of using N, I can use the mass here and the mass by molecular weight could be down here. So, this could be something like mass here by V and molecular weight and this is pi, so molecular weight of component two okay.

So, this can be written as molecular weight of component two is R T concentration of based on the mass concentration basically mass concentration divided by pi. So, if you have a means to find out pi you can also find out the molecular weight of the component something which is very useful for obtaining the information of protein molecular weight if we can observe the osmotic pressure and something which we can do in a simple exercise to get the understanding of this okay.

So we will do an example but let me just make a final note here, now, if you very carefully see this equation looks like simply like PB is equal to NRT kind of equation. So this is kind of a similar form of idle gas equation of state okay.

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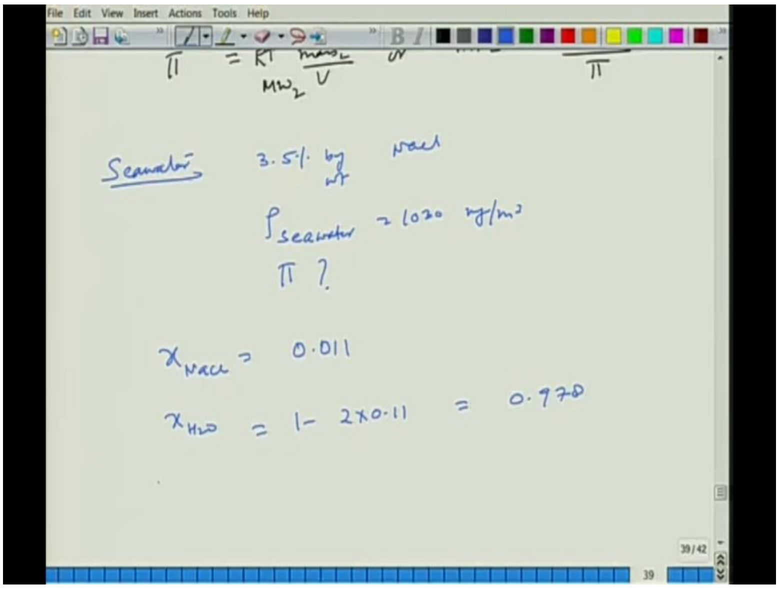


$\Pi = RT \frac{mass_2}{MW_2 V}$ or Π

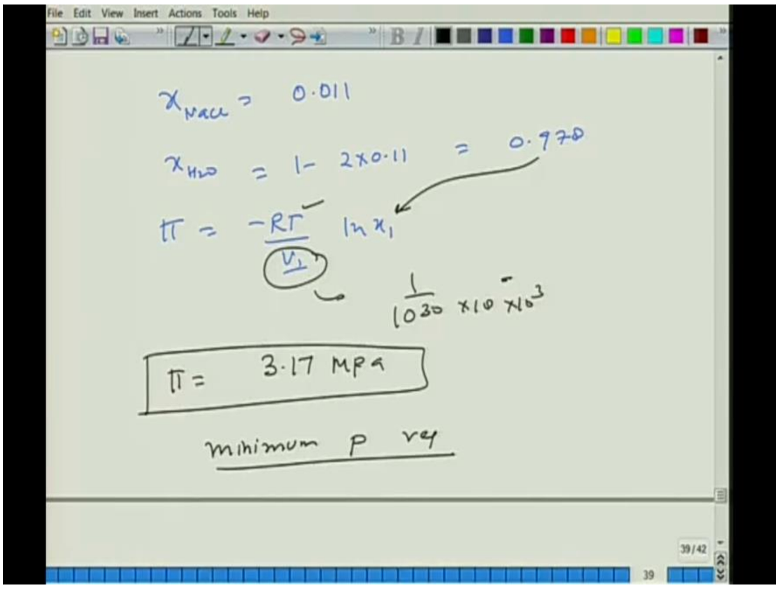
Seawater: 3.5% by wt NaCl

$\rho_{seawater} = 1030$ kg/m³

Π ?

$x_{NaCl} = 0.011$

$x_{H_2O} = 1 - 2\times0.11 = 0.978$



$x_{NaCl} = 0.011$

$x_{H_2O} = 1 - 2\times0.11 = 0.978$

$\Pi = -\frac{RT}{V_1} \ln x_1$

$\frac{1}{1030} \times 18 \times 10^{-3}$

$\boxed{\Pi = 3.17 \text{ MPa}}$

minimum P req

So, let us look at an example again, here again this is sea water. And the question is that if you are considering 3.5 percent weight NaCl by weight right and if you are considering the density of the sea water as 1030 kg per meter cube then what is the pi for seawater? What is the necessary pressure in order to have this reverse osmotic membrane working minimum pressure that we can do, but note that seawater does have more than the sodium salt here or NaCl so but we are just considering NaCl to start with.

So whatever extra so basically the first thing of course the first thing we have to do is to get the composition of NaCl okay this we can do that by simply the other way around which we have done. So based on that if we look at the earlier example it is 0.011 so something which we have done so we simply write this here.

Now, of course, we know that we want to dissociate completely so in that case the x H 2 O composition would be 1 minus 2 into 0.11 that would be 0.978 right. So pi could be written as simply this here so this we can write it x 2, x 2 would be 0.022 right or we can write here if we are considering this gamma to be 1 directly x 1.

So, if we are using this developed condition, I can also write this as minus P V 1 bar ln x 1. So x 1 is this temperature we know and molar volume for 1 would be simply 1 by 1030 that we can approximate okay and multiply that by of course 18 and this is something which we will get. And this is your kg per meter cube right so and this molecular weight is 18 gram per mole so we can obtain this by multiplying with 10 to the power 3. So, if we put this information, the amount we got for the pi turns out to be 3.17 mega pascal okay.

So this is the minimum pressure required okay usually because of the presence of other component the amount of pi which is needed in order to maintain this reverse osmotic condition would be much higher. So, alright you got the idea of at least this aspect of it, so let me also spend bit time on this interesting problem of finding the molecular weight okay. So, if you are able to use some experiment to obtain the pressure. So, this could be something like usual measurement for osmotic pressure for protein solution.

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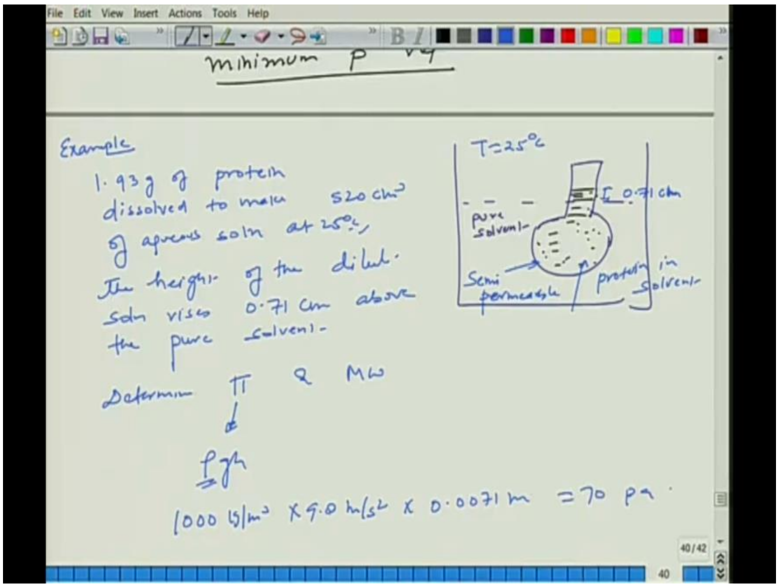

minimum P req

Example

1.93 g of protein dissolved to make 520 cm³ of aqueous soln at 25°C, The height of the dil. soln rises 0.71 cm above the pure solvent.

Determine π & MW

$\pi = \rho g h$

$1000\ kg/m^3 \times 9.8\ m/s^2 \times 0.0071\ m = 70\ Pa$

So it is something like this, you have that is the solution okay. This is a pure solvent and if you can have a protein solution in a semi permeable membrane which has got something like this okay. So if you have a membrane then if you this is the protein solution when you put it in this particular pure solvent the solvent the protein solution the protein solvent okay so this may rise to a certain height.

So this is something which is dipped in this pure solvent. Now, being this semi permeable at equilibrium there must be some head we should develop here the let us say that point is 0.71 centimetre okay. So, if this is the case for your system at a temperature of 25 degree Celsius, in such a case one can also find out the molecular weight for protein in this particular solvent.

So this is a an example again where the information is the following that you have been given 1.93 gram of protein dissolved to make 520 centimetre cube of aqueous solution that means this protein dissolves in water at 25 degree Celsius, and of course the height after the dilute solution after the you know putting this particular equipment okay which consists of this semi permeable membrane this particular solution rises by 0.71 centimetre above the pure solvent okay, so the height dilute solution rises 0.71 centimetre above the pure solvent .

So the question is determine pi and molecular weight of the protein? So pi is very straight forward, pi would be simply the rho gh so this is going to be rho gh. Rho is that of the solvent which we are going to consider a 1000, if we consider 1000 kg per metre cube and g as 9.8 metre per second and say h as 0.71 centimetre that will be a 0.0071 metre then this going to be 70 pascal okay. So that will be your pi okay.

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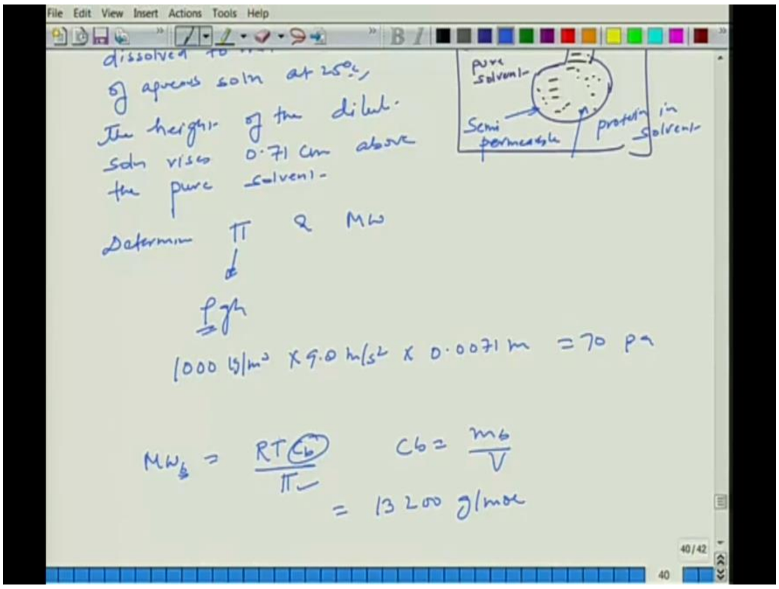

dissolved to

of aqueous soln at 25°C,

The height of the dil. soln rises 0.71 cm above the pure solvent.

Determine π & MW

$\downarrow$

$\rho g h$

$1000\ kg/m^3 \times 9.8\ m/s^2 \times 0.0071\ m = 70\ Pa$

$MW_b = \frac{RT\,\boxed{C_b}}{\pi} \qquad C_b = \frac{m_b}{V}$

$= 13200\ g/mol$

Now, what about your molecular weight? So that could be your, the other expression which we have got R T C b that is for the solute. So, if we are using solute here then this will be a pi so b is a solute, we can use 2 also. So, pi we have calculated what about C b okay C b is mass of b which is given to you because it is 1.93 divided by total volume that is the concentration of the solute, pi we know T we know R we know so we can find out MW which comes out to be 13200 gram per mole okay.

So, this is how we are going to solve something like this kind of a problem but one of the assumptions I must say that we have taken here we have approximated the density of the solution by the density liquid density of the water at this condition okay. So, that will be the end of this coagulative properties completely and I think we will stop here. We, will take up another problem or another topic in the next lecture. See you in the next lecture.