Indian Institute of Technology Madras

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Chemical Engineering Thermodynamics
by

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Lecture 30

Thermodynamics Consistency/ Reverse Osmosis

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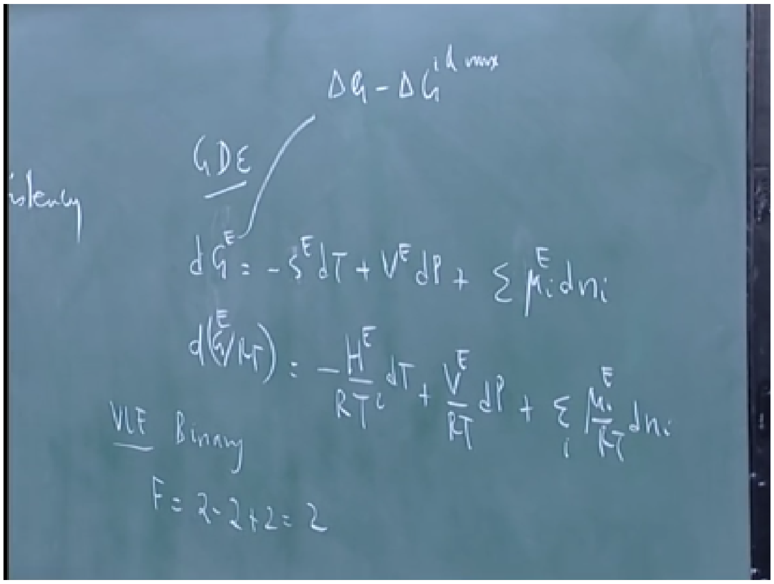

$$\Delta G - \Delta G^{id\ mix}$$

$$dG^E = -S^E dT + V^E dP + \sum \mu_i^E dn_i$$

$$d(G^E/RT) = -\frac{H^E}{RT^2} dT + \frac{V^E}{RT} dP + \sum_i \frac{\mu_i^E}{RT} dn_i$$

$$F = 2-2+2 = 2$$

Yes, I do not think I did thermodynamic consistency you mentioned it reverse osmosis, and then boiling point elevation, and freezing point depression okay. We will discuss thermodynamic consistency first, the idea is the following. If you look at the Gibbs-Duhem equation looking at I will write the expression d gE/RT, this was not like this in capital letters or dG/gE I mean Δg-Δgideal mix.

The students have come, if you are looking at vapor-liquid equilibrium let us say in particular you are looking at a binary system. The number of degrees of freedom is simply 2-2 + 2, two phases.

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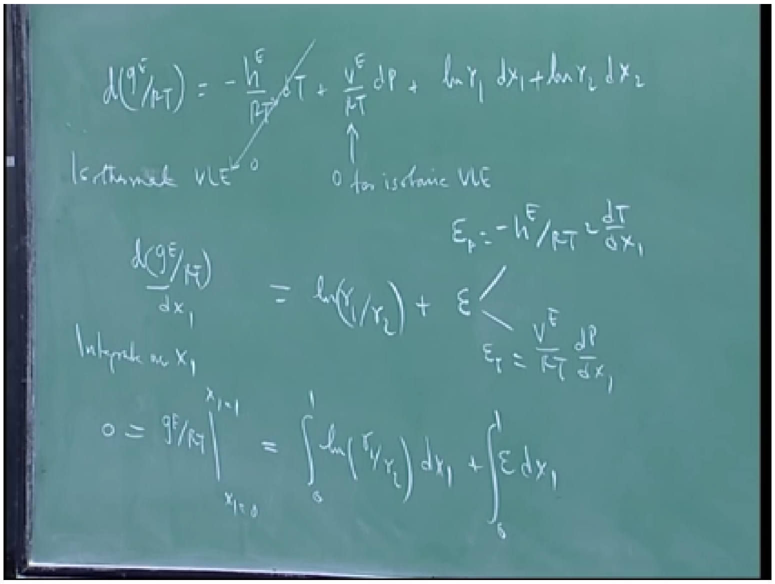

$$d\left(\frac{g^E}{RT}\right) = -\cancel{\frac{h^E}{RT^2}dT} + \frac{v^E}{RT}dP + \ln\gamma_1\, dx_1 + \ln\gamma_2\, dx_2$$

Isothermal VLE $\rightarrow 0$

$\uparrow$ 0 for isobaric VLE

$$\varepsilon_P = -\frac{h^E}{RT^2}\frac{dT}{dx_1}$$

$$\frac{d(g^E/RT)}{dx_1} = \ln(\gamma_1/\gamma_2) + \varepsilon$$

$$\varepsilon_T = \frac{v^E}{RT}\frac{dP}{dx_1}$$

Integrate over x_1

$$0 = g^E/RT\Big|_{x_1=0}^{x_1=1} = \int_0^1 \ln(\gamma_1/\gamma_2)\, dx_1 + \int_0^1 \varepsilon\, dx_1$$

And so I can write this as d(gE/RT) first of all is equal to – hE/RT^{2}dT+VE/RTdP+μE/RT is exactly logγ1dX1-logγ2dX2. Remember this μE/RT, this μ-μiideal, this is simply logγi. And if I divide by the total number of moles dividing it for a closed system if I divide by the total number of moles and I simply get logγ1dX1- logγ2dX2 no plus sorry, no minus here this is plus.

Since there are two degrees of freedom there are either you can consider isothermal VLE in which case this term is 0 or this is 0 for isobaric, many case you get d(gE/RT)/dX1 = logγ1/γ2 (logγ1-logγ2)dX1, dX2 is –dX1 + εdX1, I am sorry just ε, where ε is either, ε is hE/RT^{2}-hE/RT^{2}dT/dX1 or it is VE/RT dP/dX1, two degrees of freedom so the degrees of freedom that I use either I do isothermal VLE in which case temperature is constant, the other variable is X1.

So if I treat P and X1 as variables in a system with two degrees of freedom dgE/dX1 will be this plus ε where ε is simply VE/RT dP/dX1. So sometimes written as ε T this is usually written as ε P and this is ε T this means at constant temperature ε is VE/RT dP/dX1. Now if you integrate this over X1 the left-hand side is simply dgE/RT from X 1 = 0 to 1, so you will simply get gE/RT, from X1 = 0 to X1 = 1 this is equal to integral 0 to 1 log(γ1/γ2) dX1.

This left hand side is clearly zero, left hand side is simply gE at X1 = 0 and X1 = 1, so it is clearly equal to 0.

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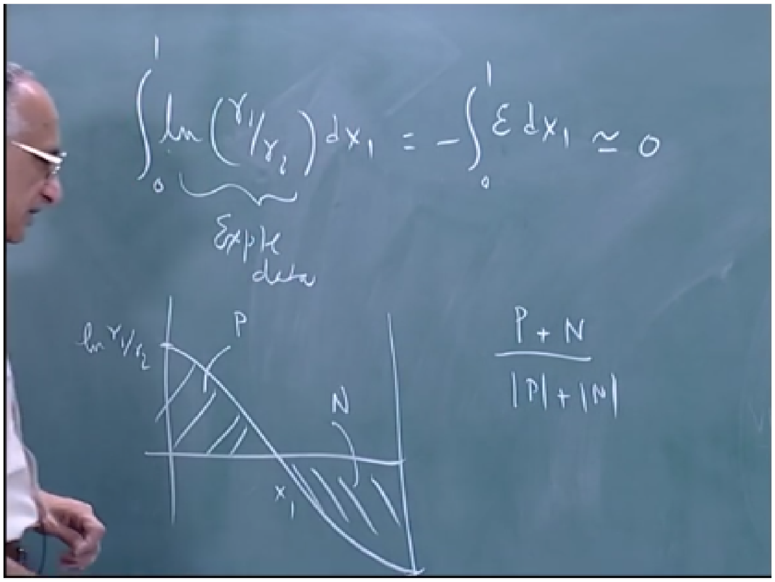

So you get the conclusion that log γ 1 by γ 2 dX1 integral 0 to 1 should be equal to go to – 0 to 1 ε dX1. Now this term is approximately zero experimentally hE/RT^2 is very small and so is VE/RT, both these terms have usually small, so you get the integral of this over dT dX1 to dX1. So because these that is why the symbol ε was used, because this is approximately zero this is a test of consistency.

If you have data experimental data on γ1 for example you can get calculate γ1 from experimental measurements and pressure, composition of the gas phase in compression of the liquid phase. So this comes from experimental data if you have experimental data on γ1 γ2 you can plot logγ1/γ2 versus X1, the area under the curve should be approximately 0. Actually, if you actually do the plotting go get logγ1/γ2 versusX1.

If you go to X1 going to 0 γ2 is 1 you get logγ1 ∞ that will be the limit here, so let us say logγ1∞ somewhere here and logγ2∞ is here. So you will get a curve like this, this area there is a positive area and a negative area this area will denote this area by P this area by M to indicate positive and negative areas. So the experimental, the integral test for thermodynamic consistency as I told you earlier people used to use the experimental data to verify the Gibbs Duhem equation.

Now the Gibbs Duhem equation is so well established that they test for consistency of the data have you measured the data correctly you measure y1 x1 etc, if you have errors in the measurement then it would not satisfy the integral test.

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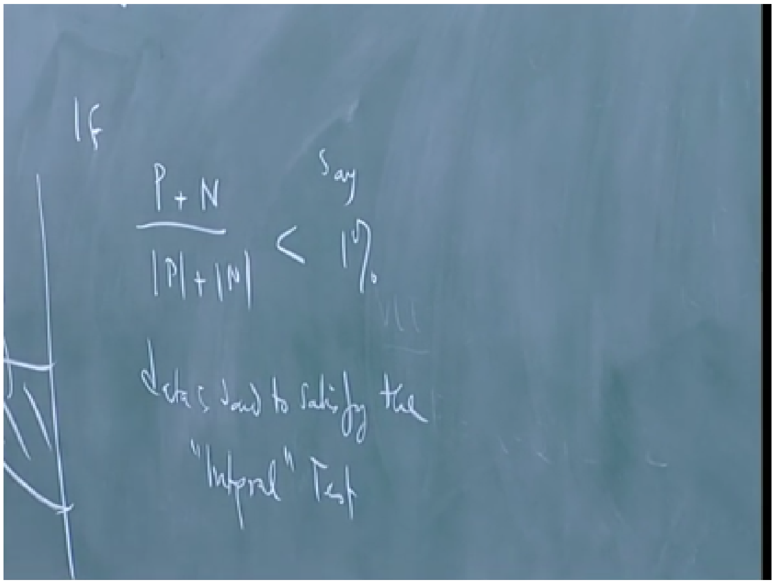

If

$$\frac{P+N}{|P|+|N|} < 1\% \quad \text{say}$$

data's said to satisfy the
"Integral" Test

The integral test says if P is the positive area and N is a negative area P+N/P+N this is algebraic quantity that is a negative area, this is the positive area is less than a prescribed amount say 1% depending on the, if then data is said to be consistent, said to satisfy the integral test this test is called the integral test of consistency, because you are taking an integral over the entire composition test.

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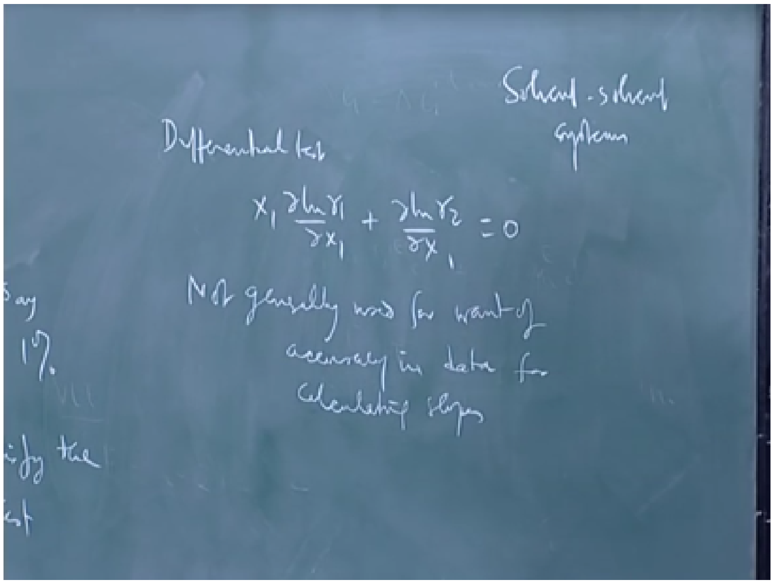

The original differential test is simply this of course this is almost never satisfied by the data simply because it is too hard to apply. This is your Gibbs Duhem equation, if you can verify at every point that this sum is 0 that is called the differential test usually differential test is satisfied to + or - 20%, because you have to plot logγ and take the slope with respect to X1, these slopes are very difficult they scatter in the points will be so much they be very difficult for you to get an accurate slope.

So this differential test is due to Van and somebody, but this is normally not used for want of accuracy for calculating slopes, this possible there are instances of data there is a journal called journal of chemical engineering data. This has a large number of data it will be it is exceptional cases where the differential test will be applied, but the integral test is almost always apply. This goes on the name of thermodynamic consistency and experimental data will always, whenever you report experimental data you have to show that they satisfy the integral test.

Otherwise, they would not even accept it for publication. This is one thing I wanted to discuss the other issues this is all this is for solvent-solvent systems. And I have discussed it for binary you can actually discuss it internally and so on there as far as you are concerned you just need to know what is thermodynamic consistency and how you test a binary system for data.

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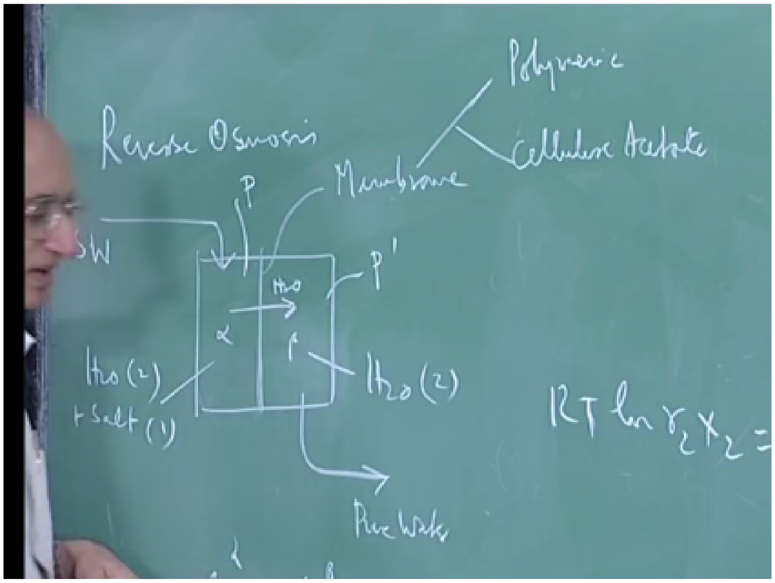

The other emission as I told you is reverse osmosis is far too important the process is also a nice plant in a place called Narippaiyur it is in near Madurai it is a beautiful plant BHEL has constructed this plant. What it involves is taking the, there they are using grid power not photovoltaic, I am suggesting photovoltaic, because grid power is also in short supply in India also drinking water supply is a need that is distributed there is no point in saying I will have 300 million tons of drinking water here in Chennai.

And then I will supply it to obscure village it will never get there. So the whole idea is to have a series of plants and one of the biggest problems in reverse osmosis membrane. Let me just described the thermodynamic principle then I will describe the plant for you. Let us say you have a membrane as usual thermodynamics says do not have to be practical you can make drawings just to indicate this is a membrane the process.

So I have here I want H2O + salt here this component 2, this is component 1, this is just pure water. Ideally what I would like is seawater to come in and for me to take out pure water. Typically the TDS the total dissolved solids and water that you drink is about 300-400 is very acceptable for portable water, but TDS in reverse osmosis water will be about 60, 70 very low less than 100.

And if water has very low TDS it is said to be very soft and it is a excellent solvent. So very low TDS water cannot possibly pass through mile steel pipes, and the curious thing about Narippaiyur is the following the state government wanted this is a backward village and they wanted drinking water supply for this. So they put up an experimental unit techniques quite a large unit. I think it is almost 1 million liters per day, and they set up this plant BHEL set up this plant it is a reverse osmosis plant.

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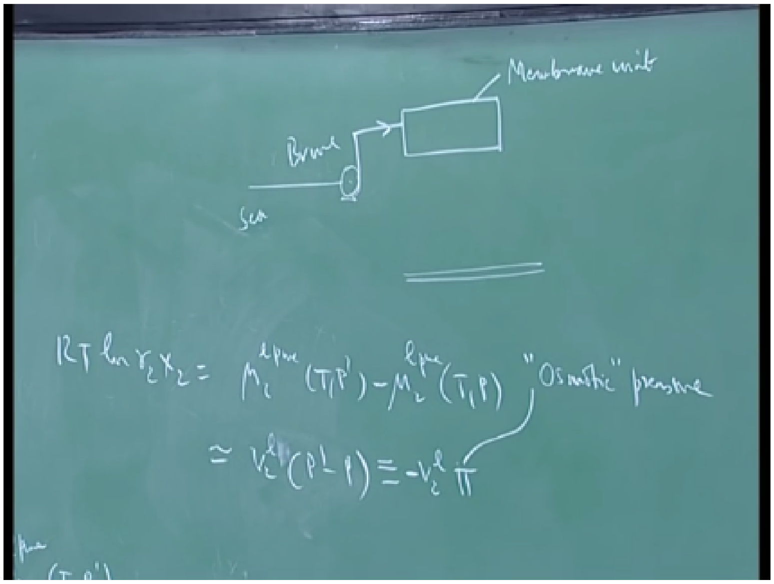

$$RT \ln \gamma_2 x_2 = \mu_2^{l\,pure}(T,P') - \mu_2^{l\,pure}(T,P)$$

"Osmotic" pressure

$$\simeq V_2^l (P' - P) \equiv -V_2^l \pi$$

So what you do is take brain the process is something like this I would take brain from seawater, you will have a pump that pumps this out, this is sea, this brain has passed through a lot of processing the final unit is a membrane unit, you should have brought you know if I have, I left my stick and you see, I have photographs of this membrane and I will show you the membrane unit essentially consists of tubes.

Because you need very large surface area each of these, there are tubes like this inside each of the whole thing is a cylindrical tube of about 1 foot diameter. The one you have here in the hostels about 1 foot within which there is a large number of tubes made of membrane semi permeable membrane. The semi permeable membrane is such that it will let water through and no salt through.

So if I am doing an equilibrium between these two faces for at thermodynamic equilibrium you have μ2 on that this is α, this is β, α = μ2β, for the moment let me assume that in fact the pressures will be different let us assume the pressure here is P and the pressure here is P', the temperature is T μ2α is the chemical potential of water. So I have to write the chemical potential of water in the mixture.

So it will be at T and P + RTln γ2 X2 that is the chemical potential model for water in solution. On the right hand side it is pure water so it is μ2 pure I do not need α here sorry, this is liquid μ2 liquid pure if you like, this is also μ2 liquid pure, but this is at T and P'. In fact if the pressures were the same these two will cancel you will get logγ2 X2 = 0, so γ2 X2 = 1.

So X2 will be 1, which means essentially what will happen is if they were at the same pressure all the water will come this side, it will keep diluting the solution till it gets more and more dilute, and all the water will be on the side you actually wanted the other way wrong. Te equilibrium process will cause water to come back in here.

So you need a pressure difference P – P' to drive the water this way that can be calculated from here you get logγ2, I complete that picture in a minute logγ2 X2 is equal to this minus this it is equal to μ2 liquid pure at TP'-μ2liquid pure T and P, you know Δμ2/ΔP is simply the specific volume of the pure substance, and water is practically incompressible, so this is simply V2 liquid pure, V2 liquid into P'-P.

This is written as V2 liquid into Л with a minus sign, because P – P' is called the osmotic pressure, so there is three lines it is a definition P – P' = Л, and Л is called the osmotic pressure. Yeah, now this is all right, now this one is RT here thanks. You can get an idea in practice you have to take γ2 into account.

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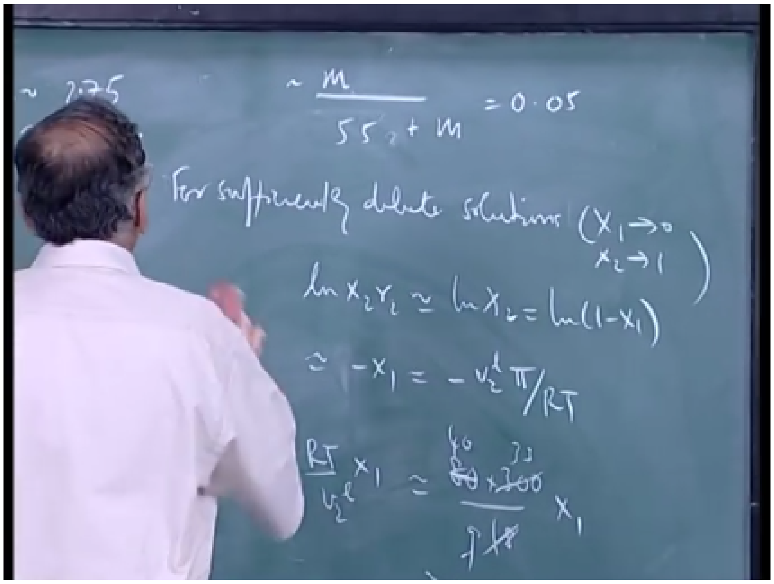

~ 2.75

$\sim \frac{m}{55_2 + m} = 0.05$

For sufficiently dilute solutions ($X_1 \to 0$, $X_2 \to 1$)

$\ln X_2\gamma_2 \simeq \ln X_2 = \ln(1-X_1)$

$\simeq -X_1 = -v_2^l \pi / RT$

$\frac{RT}{v_2^l} X_1 \simeq \frac{\overset{40}{\cancel{80}} \times \overset{33}{\cancel{300}}}{9\cancel{18}} X_1$

But for the moment let us just assume for sufficiently dilute solutions and seawater is not really sufficiently dilute you have to actually do the calculations with γ2. Dilute solutions your logX2 logγ2 X2 is approximately logX2, because X2 is approximately 1, X1 goes to 0, X2 goes to 1 tending to 1 not exactly the limit. So this γ2 becomes 1 when X2 goes to 1, so you get approximately logX2 which again is equal to 1 - X =1 sorry, log(1-X1) which is –X1, which is approximately –X1.

This is equal to –V2 liquid into Л/RT, so your Л, the osmotic pressure is RT/V2 liquid interaction to give you an idea of the order of magnitude let us calculate this in atmospheres RS for this system 80, approximately 80 temperature let us take room temperature by V2 liquid is 18 X1 to mole fraction of salt. How much does this come to, this is 9 40, this is about 33, 1300 X1.

If your mole fraction of salt is 0.1 you are talking of 130 atmospheres pressure. Actually, typically for salt water, for seawater the osmotic pressure is about 75 atmospheres. So the engineering challenges you have a semi permeable membrane this membrane by it is very structure. For example, there are two kinds of membrane say that polymer membranes are made by Dupont.

So actually, the first manufacturer of these membranes has Monsanto. Now the largest manufacturer is Dupont and there many other companies many are hidden Duponts they are all subsidiaries and so on. And then there is cellulose acetate membrane, I forget the polymeric membranes exact name, there is a polymeric one and there is a cellulose state. This is non biodegradable, this is degradable this is biodegradable cellulose state.

The membrane has cannot have pinholes if you have pinholes you will get all the salt water coming through, so you are talking of a membrane that does not permit, salt through but permits water the size difference after all is quite small, between sodium chloride in water. So you are talking of membrane that has, it is like a molecular filter, it filters out the sodium chloride sends the water through.

But it also has to withstand in a pressure of about 70 atmospheres just typically X1 will be about you can calculate X1 70/1300 7/130 4.25% this is for X1 0.05, if it is sodium chloride you are talking of X1 as moles of sodium chloride into what is the molecular weight of sodium chloride

NaCl is what 58.5 okay. Let us say approximately 60 if you are calculating moles if M is the molality it means its moles per 1000 grams of solvent by 1000/18, X1 is simply M/ by this sorry.

Now this is correct M/60, no this is moles per 1000 grams of solvent, so plus M, I am sorry. So if this is 0.05 this is about 550 0.05, so M is what, M is approximately 55x0.05 0.275 now 2.75 grams per 1000 grams of solvent or into 60 would give me 120 + 45 = 165 grams per 1000 grams of solvent, roughly 15% by weight, so seawater is that composition. So you get about 70 atmospheres for this and for 70, I just think this is about 70 atmospheres for seawater for brackish water that you take from the ground the value comes to about 20 atmospheres.

So reverse osmosis plants will differ, because you have to have a membrane that is mechanically supported it is usually supported with metallic or ceramic supports which will essentially still allow this water to come through the membrane should there it should not have holes you have maintenance problem continuously. Right now we do not have a membrane manufacturing unit here you must know that these membrane units are also used in dialysis.

We have actually done a piece of work here you just mentioned that to you because it is an interesting problem for chemical engineers on a large scale is much harder to try, but let me explain this.

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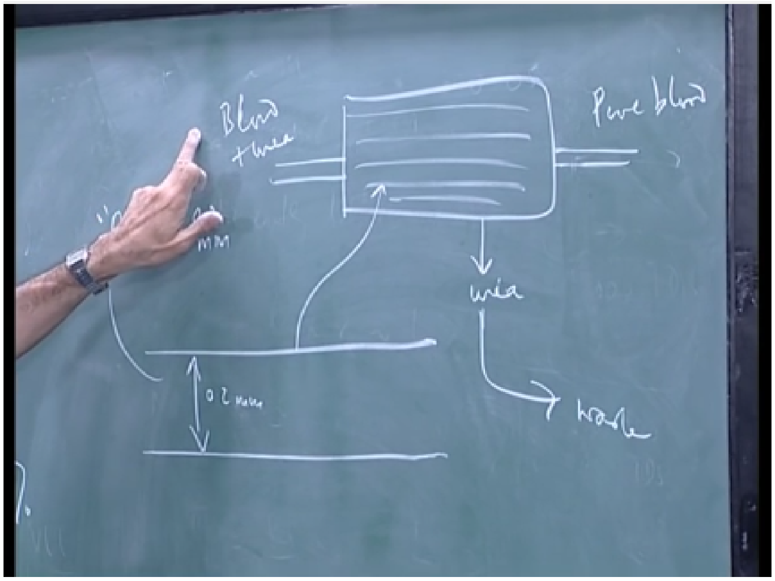

The membrane units are like this I will get you a picture of this and this is each of them is called a lumen and each of these is millimeters in thickness I mean this each lumen is only about one millimeter in radius, so you are talking a very thin membranes which are kept all over the place there will be 1000s of them in one bundle and all of these will be inside a shell.

So what will happen is you will have a tube like this, they say this is the inlet, this is the outlet you have series of tubes through which liquid will pass the shell side you will get out the water alone will come out, this is sea water pure water will be taken out here, this will be concentrated brain. Now this unit is there in your hostel what you will see is the outside shell, the ceramic shell water that comes out is concentrated brain.

In your case you are actually using your not bringing in seawater you are using brackish water. So we have a bore well that except the water that said something like 800 TDS. And then it goes through this unit, this will come out much higher concentration you can calculate by mass balance, this will come out at about 40. The problem with reverse osmosis is it would not give you, it insists on giving you a certain quality of water you will get 50 60 TDS.

Although you are satisfied with 300, the membranes do not make that compromise the membranes will give you 60. But let me come back here this membrane the question is the same thing happens in the case of dialysis artificial kidney in the artificial kidney this is your blood, plus urea, blood containing urea here you get pure blood out, here you get urea out which is a waste.

In this case you do not have this problem, these are the lumens inside each lumen looks like this it is called a lumen and each lumen is about 0.5, 0.2 mm diameter 0.2 mm varies the main advantage of a small large number of small diameter tubes is surface area you get that is what gives you the productivity. So the urea is removed and wasted urea is a larger molecule than any of the most of these chlorides.

So what they actually do is they use a dialysis set outside the solution outside the pipe will be identical with blood except for its urea they do not need the blood consists of also proteins, proteins would come through anyway. So you can leave the proteins out, but all the other components you will match the composition of the individual blood. So they have this with labeled with the patient's name because it is reused.

And the outside solution is prepared exactly to the same specifications as this blood here except for the urea. So the only thing that will come out of this thing is urea, and there is a rule that not blood should not touch any of the other parts. So the whole thing is done in PVC this thing which is known to be biocompatible, a special PVC material is used for the piping, and when the blood is taken out it goes directly into this there is a peristaltic pump.

The way you pump this is a pipeline the tube goes through this the tube from the patient will go through this, but there is a carnot meant as this rotates every time it will pinch thee my drawing is terrible of course. These are two solid surfaces as it pinches it as it rotates it will pinch it and send out a pulse. So these pumps these peristaltic pumps are used for this there is no contact of the blood with any other reason okay.

So the reverse osmosis is a very important part, and I think for desalination it is going to be the way to do it, because one of the most reversible ways of, you can calculate the work here. The work here is simply the volumetric flow times the pressure difference right WS is simply Л times the volumetric flow V.dot flow. And you can calculate that work, you will find that is much smaller than the comparable processes of evaporation for evaporation here to supply 540 calories per gram.

And for freezing you have to still supply 80 calories per gram, in addition to that for freezing you have a unit, you have the Carnot efficiency because you have to you are essentially talking about heat pump. So if you take that into account you will come back to 540, but with multiple effective operation you can do with about 50 to 60 calories per gram, here it is even less, because the osmotic pressure you are talking of flow per gram you are talking of 118.

All you have to do is take one gram of the flow which is 1CC in 2Л 70 atmospheres. So 70 into 70CC atmospheres, 70CC atmospheres will come to what less than two calories as compared to 50 calories if you have a multiple effect evaporator with a factor of 10. So in principle this should be much less, but there are hidden costs when you make comparisons like this you have to take the energy for making the membrane you are paying there right, here it is less. But you have take the membrane manufacture plus this two together to find out what the costs are.

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