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Chemical Engineering Thermodynamics
by

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Lecture 31

Miscellaneous topics in

Phase equilibria

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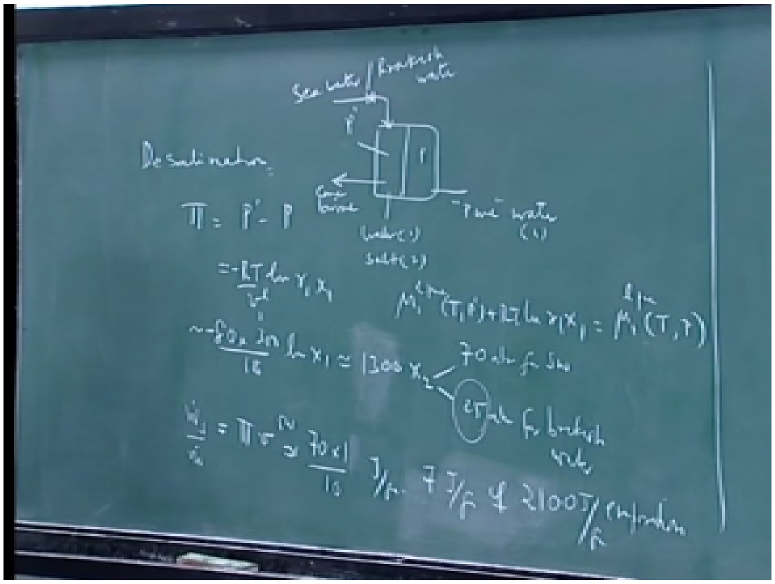

Discussing desalination and told you that the osmotic pressure is P’- P and I said the membrane units here the reverse osmosis units here do not you see water they will use brackish water, here you get pure water, water is very soft typically below 100 ppm TDS. And this pressure we found was equal to RTlog of, let me call this is here this is water which is component 1, plus salt, this is component 2, and this is component 1.

So this is μ1 liquid pure minus these will break this down P and P' this minus this is V into Л RT/V you calculated the osmotic pressure this is typically working in CC atmospheres you are working in atmospheres this is typically I suppose I should use 80. Now 80, the temperature of 300°/18 into logX1 + logX1 is 1 - X2 or the log(1-X2) which is -X2, is a minus sign from there, yes this is a minus sign which is approximately this 18 to 300/18 is about 1250, 10%.

So we said typically this is 70 atmospheres for seawater and about 25 atmospheres for brackish water. There is only an estimate simply brackish water from the ground and your membranes here are designed to withstand is 25 they are not meant for seawater we also have one unit for seawater desalination if you want to take a look at it you can in CC, that center that project that I told you about surya gel.

And if you contact some of you are interested you can ask Dr. Kumaravel where you fix an appointment with him he will show you the unit he is got a PV photovoltaic for electricity generation that power is used to drive the reverse osmosis. The reverse osmosis is the major this thing is to pump the sink to P' pump your seawater to C' P' that is from one atmosphere it will go to 70 atmospheres.

And he works at 500 liters per day so he actually buys the sea water in time. So it is filled and it is pumped and the pure water is taken out of course you will also have to take out the concentrated brain and this portion of this is a problem. And the many problems first is the membrane cost, as I said most important thing about the membrane is in India I think the most important thing is biodegradability.

And the fact that we should manufacture it otherwise it is the Japanese who manufacture it. So they will sell you the whole desalination unit for 5 lakhs or something you will be thrilled and then the membrane will be 10 lakhs every replacement. And then you will be stuck with it, I mean it is just a manner of speaking what I mean is that components will be very expensive, so you have to manufacture the membrane yourself.

To manufacture the membrane economically it requires a very large unit, so you need a large number of miscellaneous events, so it is all coupled all the states have to come together they must all agree on using the same membrane. So there is lots of coupled non-technical issues, but the crux of the matter is that we have seawater and so on and the sun in plenty energy from the Sun.

Those are only two things we have in plenty nobody can take it away from us. So we may as well use that, the thing I pointed out was that WS dot the rate at which work is done per unit produced would be ЛV for example, Ws dot/M dot. So just be ЛV which would be for seawater osmosis it will be 70 atmospheres into 18 CC per gram mole. If you are doing this in joules it is about 80 CC atmospheres 8 joules, so divided by 10 if you like roughly this is joules per gram mole.

So this is about 130 or if you are doing it per gram actually it is even into one, and just put 1 per gram. So this is about 7 joules per gram can you compare this with 540 calories in fact that is joules is even more we are talking of 210 about to 2,000 hundred joules per gram for evaporation and for freezing if you want to take out water by from saltwater by freezing out the ice you can do that it is called a one-off process was introduced in Japan way back more than 60 70 years ago.

That will be about 80 calories per gram or about what 320 joules per gram this is freezing. Actually I put down figure symbolically the 2100 has to be modified we have what is called multiple effect evaporation you will read about it. So there you can recover most of the latent heat therefore, it will come to about 210 you can get a steam what is called a steam economy of 10 that means for every mole of water evaporated in the boiler you can actually by decreasing the pressure you can evaporate 10 moles of water at various stages.

Because you evaporate 1 mole that condenses when it condenses use the latent heat to heat another gram of water. So this is done very effectively so you can get economies of about 10, so 210 and here you can get an economy of about 3, because there, there is increasing you have to first produce a cooling plant and there you have a Carnot efficiency limitation. Therefore, eventually the source of energy is the Sun.

So really here you can produce an economy of about 3 here, you can produce an economy about 10. So you are talking of 210 joules per gram in practice and here you are talking about hundred joules per gram. In spite of that of course there are many other complications here because the freezing unit has to be maintained compare that with 7, and even if you have an efficiency of three we are still talking of 20.

So in principle the reverse osmosis process is very, very economical, but it is sort of deceptive in all these cases when people give you arguments like this it is furious, because this implies that you have a separate membrane manufacturing unit, and there is work done in creating the membrane a lot of work done making the membrane, because these membranes it should not have pinholes.

So you were talking of membranes that will withstand and mechanical pressure of 70 atmospheres on one side, and are thin enough to allow water to pass through and not the salt, and have no pinholes in them. So it is a huge process of membrane manufacture it is well understood technology is well understood. So what you really have to do is come if you want to compare this with this or the evaporation process you must take the whole plant and calculate the energy requirements.

You will find they are all comparable except reverse osmosis is probably more efficient in principle by about a factor of about 20 to 30 % especially on large scale it can be much more efficient.

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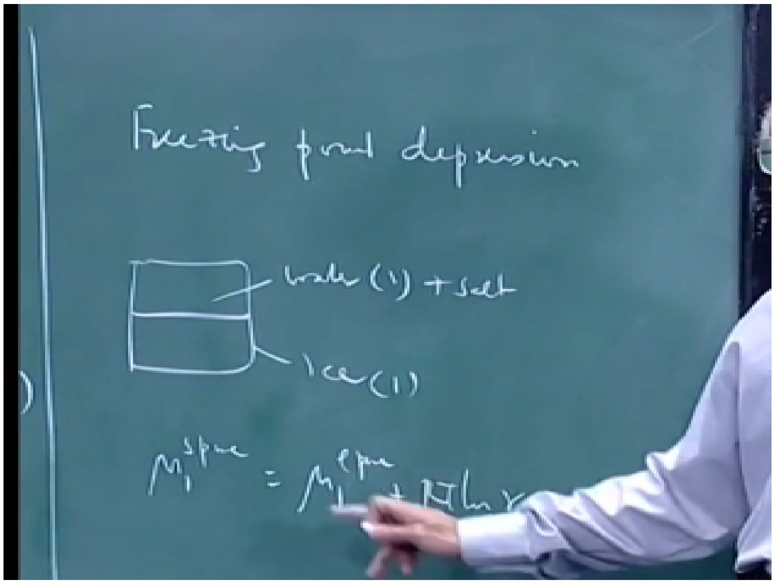

So this is as far as desalination is concerned then two other things I wanted to discuss was very similar I do not know if I already discussed this they discuss freezing point depression I am talking about water and ice, you want to lower the freezing point of ice this is not of direct day-to-day interest for us, but in very cold countries we have this ice formation they want to know if this is water component 1 + salt this is pure component 1.

Now I simply equate like all phase equilibrium problems I have only water in both faces, so I have to equate µ1 solid pure is equal to µ1 liquid pure at the same TNP + RT Ln γ1X1. Well I do not know µ1 I can relate them, but I cannot relate, I cannot get across the phase boundary directly, because the saturation pressure is where the equilibrium is. So one possibility is simply make note that saturation pressure the two are equal and apply corrections in the pointing correction.

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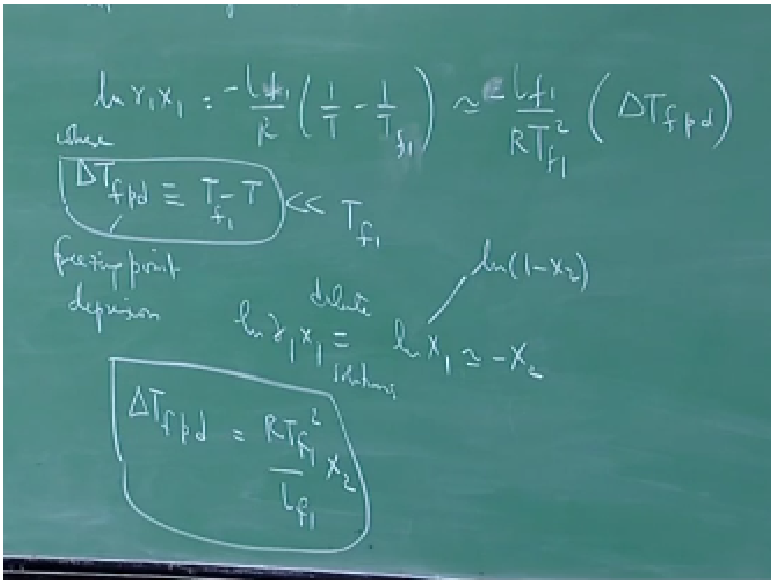

But I have told you this logγ1 X1 what I am looking at is the freezing point is equal to μ1 liquid solid pure minus μ1 liquid pure by RT it is only at the triple point that these the pure solid in the pure liquid will be at equilibrium with one another, because water does not have, it has a melting range, so I can go to the saturation pressure at which it melts, that is one possibility. But if I am not sure that I am in the correct region of phase space the easier way to handle it and also because I am interested in this case in the temperature of the freezing point.

So I am really looking at T, so I take this and differentiate this with respect to P and get h1 liquid pure - h1 solid because it will be change in sign. This will be the latent heat of melting of $1/RT^2$ this is h1 liquid pure - h1 solid pure. Now when X1 = 1 which is pure water γ1 is 1 and T should be equal to the melting point of the solid, TM1or the normal freezing point we call it TF1.

So this is the normal means at one atmosphere freezing point may be 0° C typically for what. So it is a differential equation for X1 in T γ1 you have to know a model. So you are solving it with this condition if you assume that this is approximately constant you get log γ1 X1 = LM1/R into this is X1=X1 = 0 sorry, X1 at X1 = 1 we have seen this is 1/TM1 you can say approximately if you like, because basically the latent heat of melting is also a function of temperature.

Actually you can do this rigorously also, because we would not do it rigorously you just have to know what is this as a function of temperature we will do this incidentally LM1 is strictly a function of temperature in this particular case it is in negligible change because you will find the freezing point depression is a few degrees lower those few degrees Δ h does not change. I will come back to this, let me look at this here this is the expression here since at x1 =1 γ 1 is 1 this is simply log $\gamma_1 x_1$. T is the point at which the solution freezes solution containing salt freezes, the solid phase that's produced is pure ice.

So this is the actual freezing point and this is the called it T_{M1} T_{F1} keep changing I sorry T_M same is T_{F1} this is the freezing point of water in the presence of salt, this is the freezing point of pure water, so if you have we call this ΔT freezing point depression this is freezing point depression physical chemists call it this is defined as T - T_F 1 - T and this is actually much smaller than you can verify this Δ T will be typically the order of a degree where STF oneness doing degrees K.

So this is 273 so this is typically very small so I can write this as LF1 sorry by RTF1 TF 1 into TF 1 - T so there will be a - sign sorry is a plus sign TF 1 - T is Δ T freezing point depression by TF 1 so TTF1 is actually approximately $TF1^2$ typically in these applications you try to lower the freezing point by adding a small amount of salt so X1 is close to 1 X2 is small so when X1 is close to 1γ 1 is 1.

So we have approximately log γ 1 X1 dilute solutions which is what we open is the same as log X1 which is approximately - X2 it is log of 1 - X2 and therefore just - X2 so Δ-t freezing-point depression I think I am missing a sign somewhere here LFT TF1 you get TF1 – t that is what i defined this is already or the previous one okay this is a LF again sorry log γ1 x 1 t -or there is a - sign here in the integration thanks I needed it- n – n.

So define this way ΔT freezing point is simply equal to r $TF1^2$ / LF1 x X2 actually solving a face equilibrium problem but the information you get from the face equilibria problem is seek depression in the freezing point upon addition of solute actually it has a PICC you must physical chemists use it to calculate molecular weights of polymers what they do is weigh a certain amount of polymers m2 will be the weight of the polymer they added to known amount of solvent.

So this is the expression they measure this quantity right if you make a polymeric substance you can measure this RT and L are known these are for water or for the solvent in question so if you dissolve a polymer for example in a solvent and for the solvent you know it is freezing point and it is latent heat then this coefficient is known and you know x2 from this calculation.

You know the amount of polymer you added therefore you can calculate its molecular weight if m2 is the palpable molecular weight is the total weight of polymer added two thousand grams of solution you get m2 by molecular weight of polymers divided by m2 by molecular weight of polymer plus moles of water solvents eight thousand by eighteen.

That is known therefore you can calculate the molecular weight of polymer but coming back here you can calculate the freezing point depression that you need in order to get x2, so yeah what log x one is log of 1 - X2 when X2 is small it is approximately - this one is log of 1 - X2 log of 1 - X is X- X it is a Taylor expansion when x is small so we will calculate this RTF1.

one so RTF 1 for example for water by $Lf1^2$ this is for water which is component one this will be about and do it in calories because I know LF1 in calories per gram I know $RTf1^2$ by Lf1 $Tf1^2$ 273^2 / LF one would be about 80 calories per gram this is by 80 if there is a calculate so for water plus solute ΔT freezing point depression is approximately given by this must be this must come out in degrees K because our TF has the same unit says LF what does this come to does anybody have a calculator we something like 90 to 100.

So one not for let us say 114 to approximately you can see what will happen in the case of boiling point elevation do the same thing I think I will do it on this port because I want to copy the boiling point elevation results they are very similar so let me write down first you have liquid and vapor this one is water component 1 + solute which is 2 here this is water so for the solution you will still get μ on liquid + r RT ln γ or next one.

And the other side will be μ on vapor pure instead of solid pure so you become vapor pure so you do the same differentiation instead of liquid latent heat of melting you will get latent heat of evaporation call it L1 B is called boiling point elevation, so I will call L1B but L1B will be H 1 liquid sorry paper pure - liquid pours but notice this is vapor - liquid so you pick up a - sign here because when you differentiate you will get liquid -vapor μ /T will give you a - H / T^2

This is still valid $T \neq F1 = TB\ 1$ it is normal boiling point, so this is TB1 again we will integrate assuming that this is LB1 or L1B if you like this is the latent heat of evaporation of water so you would still get this there is a - sign that has changed now because of this - sign this - sign will go so this - sign will disappear we will get TB1 you will pick up a - sign here this is called boiling point elevation is defined as T- T boiling point of 1.

Because you know the boil we turn out that the boiling point increases so T will be greater than and you want this quantity to be a positive quantity ΔT boiling point elevation it is still true that this is much greater than the boiling point of 1, so this will change to LB1 L1B by T1B so here the - sign is restored at this point.

So Δ T boiling point elevation will be RT boiling point of 1 the whole square by L boiling point of1 into X to the boiling point elevation so it is defined as T- T be 1 the other one is defined as TF1 - T so this is now called boiling point elevation so again I get I have to evaluate RTb1^{2} / Lb 1 for water this will be 2 x 373^{2} point I set is now 540 x 80 you do that for 373^{2} 540 calories per gram but 29.

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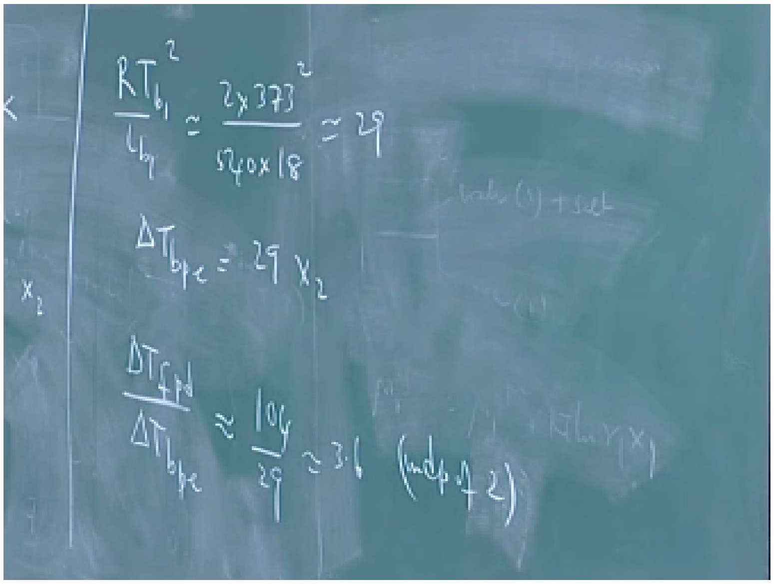

Approximately 29 into X2 into X2 of course so this is sorry this is just 29 then I have a ΔT boiling point elevation is equal to 29 X2 Δ-t freezing-point depression by Δ-t boiling point elevation that correct 16 10^{4} 323:9 okay then this buy that a sunburn 4/293.6 for the same amount of addition you get a larger depression and a boiling point elevation thank you trying to think okay.

Anyway you can see that these two are connected and sometimes this is used for consistency of measurements if you are measuring x2 for example in solution if you are measuring for the same solution you can measure your ΔP freezing point you can measure your boiling point and you can verify that the ratio is independent of x2 and dilute solutions this is independent of x2 in fact it i independent of to leave alone x2.

No matter what the solute is for a given solvent the ratio of boiling point elevation to the freezing point depression is a constant its function only of the so actually the number of such applications is any number you just have to in every situation you start with the chemical potential model for the phase if it is solid liquid or vapor and then work through it you cannot go wrong.

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