Thermodynamics of Fluid Phase Equilibria
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Lecture - 40
Models for Electrolyte Systems

Welcome back in the last lecture what we did was to look at the relation between the pressure difference across the membrane for non electrical systems. Today we are going to look into electrolyte systems which was first described in detail by Donnanand, sometimes called Donnan equilibrium as well ok.

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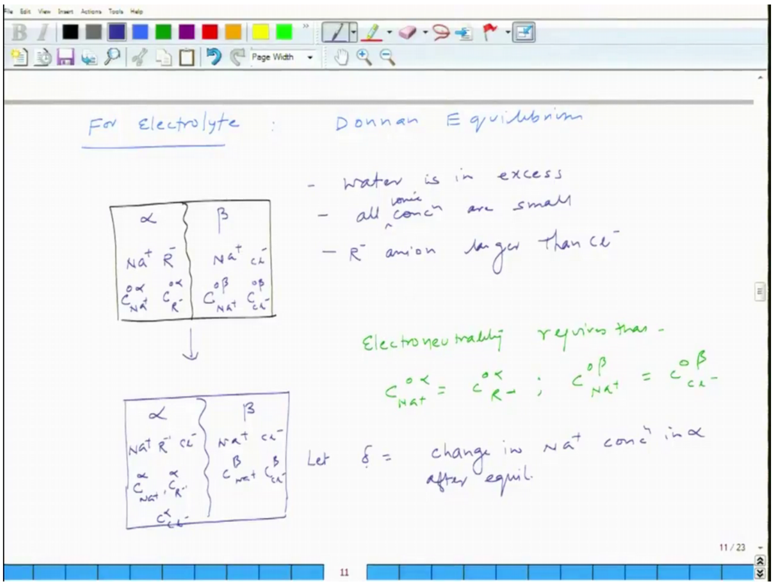

For Electrolyte : Donnan Equilibrium

- water is in excess
- all ionic conc^n are small
- R^- anion larger than Cl^-

Electroneutrality requires that -

$C^{o\alpha}_{Na^+} = C^{o\alpha}_{R^-}$; $C^{o\beta}_{Na^+} = C^{o\beta}_{Cl^-}$

Let δ = change in Na^+ conc^n in α after equil.

So, the concepts are similar but let me first go into details so that you can appreciate all these expressions which we are going to make use of it. So, remember it is not it is not important to remember the expression in the in the final state.

For the case of a Vant Hoff equation which was derived for a non electrolyte pi is equal to crt, something which we can remember why because this is a analogous to ideal gas equation of state. But what we are going to talk about for the electrolyte will be little more complicated.

So, let us consider a chamber like this a separated or divided into two parts by membrane that this membrane exhibits ion selectivity ok. And this is the reason is that many natural systems such as for example, your body have such kind of membrane which permits certain types of ions and rejects other ions ok.

So, I am going to make use of the same concept here I will say this is alpha phase and this is beta phase ok. Now this is at before equilibrium let us say you had or the system had N plus and R minus ok, and R is much larger than cl minus 1 and in this case you have N a plus and cl minus it is and the water is there. So, water is in excess and all these concentrations of this ions, are very small. So, ionic concentration are small ok.

So, this is basically a system which we are looking at it. So, let me also write this that R minus anion is larger then cl minus ok. So, what happens at equilibrium? So, since the membrane will allow N a plus N a cl minus and will not allow the R minus to come to the other side. So, certain amount let us assume that gets depleted from the beta phase and goes to the alpha phase.

So, what happens here that after equilibrium you have a situation something like this ok. So, this is again alpha beta and now I have to also mention some kind of concentration. So, initially let us say this was c, 0 alpha N a plus for the case of N a plus and this is c 0 alpha for the case of R minus alright. And this is again c 0 beta N a plus c 0 beta cl minus alright.

Now, in this case now you have N a plus R minus and as well as cl minus ok. Here you have of course, only N a plus and c l minus ok. So, what we are going to do is we are going to just define c alpha as the final state, N a plus similarly c alpha R minus and c alpha cl minus and similarly here c beta n plus c beta cl minus ok.

Now system is a electro neutral so neutral. So, essentially in the final and in the later state both would be the same. So, electron utility requires that requires that that in this case if you look at it; that means, the concentration of N a plus c 0 alpha should be same c 0 alpha R minus alright that must be maintained that is initial condition. And as well as c 0 beta n a plus should be same as c 0 beta c l minus ok. So, that is a condition which we should have alright.

Now after change we assume that some amount delta is the change in the amount of concentration in that same sodium in alpha phase so; that means some amount of sodium which we are going to say a delta moves from the beta to alpha phase. So, let me write here, so let delta is the change in sodium plus concentration in alpha after equilibrium now note that R now R minus cannot move from the left hand side to the right hand side remember. So now, sigma is changed which in the beta phase also you will have some changes in the sodium of the same amount and as well as the chlorine of the same amount.

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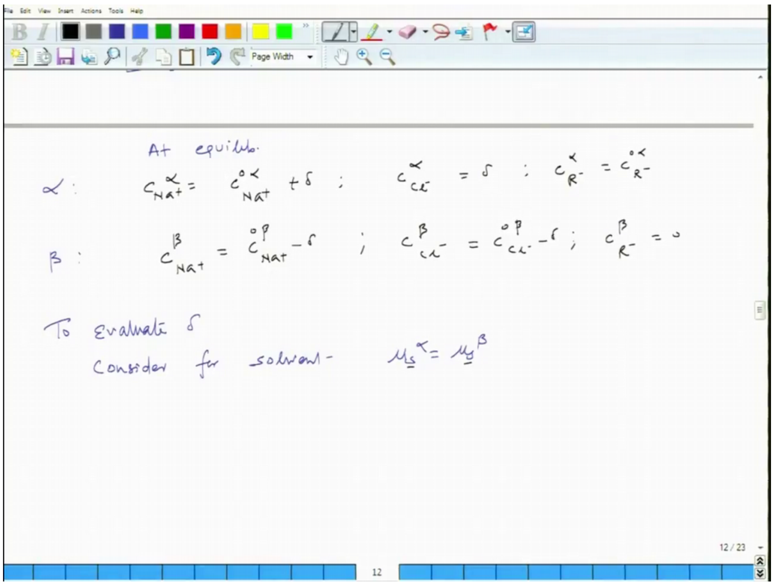

At equilib.

α : $c^{\alpha}_{Na^+} = c^{0\alpha}_{Na^+} + \delta$; $c^{\alpha}_{Cl^-} = \delta$; $c^{\alpha}_{R^-} = c^{0\alpha}_{R^-}$

β : $c^{\beta}_{Na^+} = c^{0\beta}_{Na^+} - \delta$; $c^{\beta}_{Cl^-} = c^{0\beta}_{Cl^-} - \delta$; $c^{\beta}_{R^-} = 0$

To Evaluate δ

Consider for solvent - $\mu_s^{\alpha} = \mu_s^{\beta}$

So, at equilibrium the kind of concentration which will have it is as follows where alpha c n plus alpha is c 0 alpha N a plus plus delta ok. Similarly is that it is also going to be delta and for the case of R it will remain as it is there is no change in that.

For the case of beta phase you will have c beta N a plus this is going to be c beta minus delta c beta cl minus is equal to c 0 beta cl minus minus this ok. And of course, there is no there is no r; that means, we have we can simply say this is going to be 0 ok. So, this is the condition which we have.

Now the question is how do we evaluate delta ok, so if we will evaluate delta we make use of their condition of equilibrium and we will start only with the chemical equilibrium. So, we will just look at the chemical a potential equality. So, to evaluate delta what we can do is we can consider first we will just consider the solvent ok.

So, consider for solvent mu s alpha is equal to mu s beta ok. So, at what we can do is this is just for the solvent remember ok. Now what we need to do is we need to connect to the pressure so that is what we have also done we looked into the osmotic pressure. So, we will make use of that those expressions.

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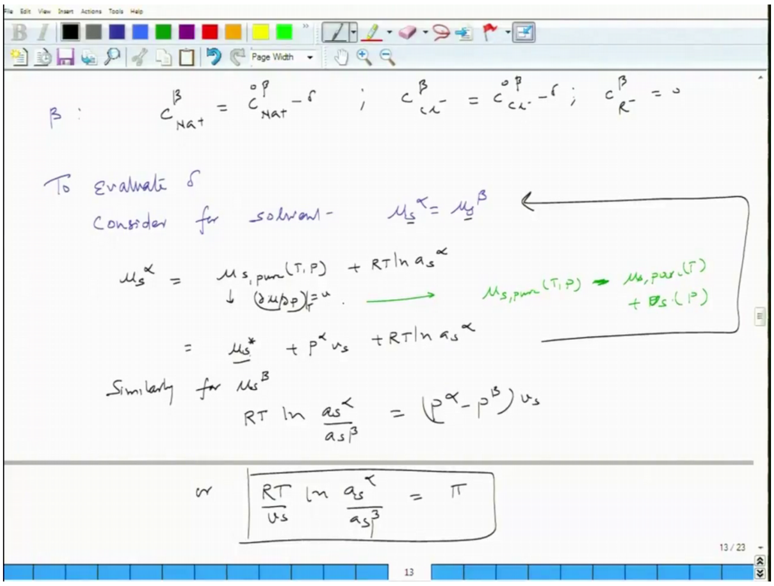

β : $C^{\beta}_{Na^+} = C^{0\beta}_{Na^+} - \delta$; $C^{\beta}_{Cl^-} = C^{0\beta}_{Cl^-} - \delta$; $C^{\beta}_{R^-} = 0$

To Evaluate δ

Consider for solvent - $\mu_s^{\alpha} = \mu_s^{\beta}$

$$\mu_s^{\alpha} = \mu_{s,pure}(T,P) + RT\ln a_s^{\alpha}$$

$\downarrow$ $\left(\partial\mu/\partial P\right)_T = v$. $\longrightarrow$ $\mu_{s,pure}(T,P) \rightarrow \mu_{s,pure}(T) + v_s(P)$

$$= \mu_s^{*} + P^{\alpha} v_s + RT\ln a_s^{\alpha}$$

Similarly for μ_s^{β}

$$RT\ln\frac{a_s^{\alpha}}{a_s^{\beta}} = (P^{\alpha} - P^{\beta})v_s$$

or $\boxed{\frac{RT}{v_s}\ln\frac{a_s^{\alpha}}{a_s^{\beta}} = \pi}$

So, let me just write down this as mu as alpha as a basic definition are connecting with the activity as mu s pure at certain temperature and pressure plus R T ln has s alpha ok. Now, this I can also use this del mu by del p a molar volume at a constant temperature and consider from p is equal to very small values 0 to certain p. And if I do that I can write this as this plus p alpha considering this to be incompressible.

So, if you integrate this right you are going to get from very small values of mu for the pure. So, this is at t is equal to t P right, so you will get it like t and P goes to 0 it is like this. If you cannot get this is like mu s pure t P is mu s pure or minus if you say pure t ok, assuming to be p equal to 0 plus v s pressure is p p minus p 0 that is id we had it.

So, we plug in here and then this is going to be R T ln as alpha, similarly this we can do for beta phase ok. And then this would be considering a solvent same conditions, so if you subtract this you is going to be basically 0.

So, you plug in this expression here and this you can plug in here and if you do that we are going to get the following R T ln as alpha divided by as beta and they should be P alpha minus P beta times v s or I can write it as R t by v s ln a s alpha by as beta this is pi. So, I got a osmotic pressure expression right.

This is the standard osmotic pressure expression based on simple analysis the key is now to connect to this other ions the concentration of the ions how do we do that. So, let me also elaborate bit. So note that just like a solvent chemical potential should be same similarly the salt chemical potential in the true phase as shown be same so; that means, mu N a cl is equal to mu Na cl.

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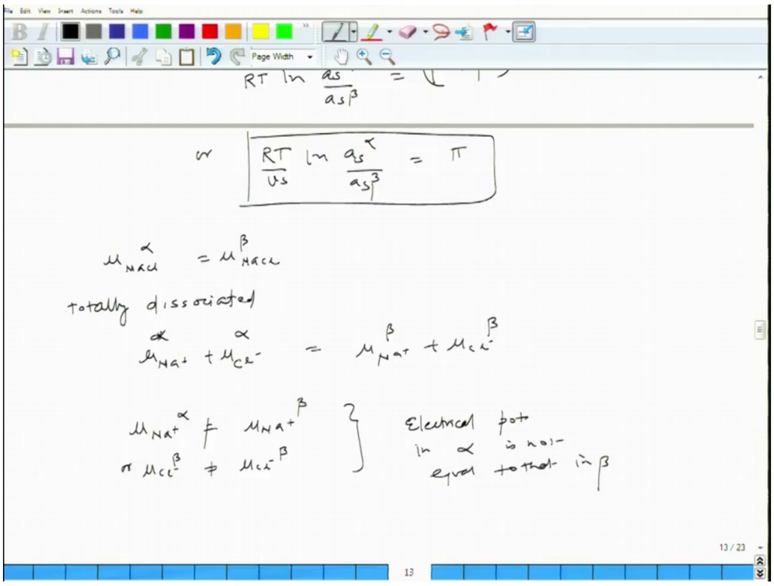

$$RT \ln \frac{a_s}{a_s^{\beta}} = (\quad)$$

$$\text{or} \quad \boxed{\frac{RT}{v_s} \ln \frac{a_s^{\alpha}}{a_s^{\beta}} = \pi}$$

$$\mu_{NaCl}^{\alpha} = \mu_{NaCl}^{\beta}$$

totally dissociated

$$\mu_{Na^+}^{\alpha} + \mu_{Cl^-}^{\alpha} = \mu_{Na^+}^{\beta} + \mu_{Cl^-}^{\beta}$$

$$\left.\begin{array}{l} \mu_{Na^+}^{\alpha} \neq \mu_{Na^+}^{\beta} \\ \text{or } \mu_{Cl^-}^{\beta} \neq \mu_{Cl^-}^{\beta} \end{array}\right\} \text{Electrical pot in } \alpha \text{ is not equal to that in } \beta$$

Now, though these dissociates so you may tend to just say that you know mu of N a plus in alpha should be same as mu of N a plus beta, but this is something which you cannot do that. Because you have as you have a salt which you are which is which is at equilibrium not individual ions there ok, so that most of the easy mistakes which we do, but you can sell it if they dissociate you can separate it out ok.

Then considering this that you are on this ion get totally dissociated, you can write like this for alpha this should be same as for beta that you can write not for individual one ok. Now what we can do is we have this expression this is an ion selectivity membrane, this is because if you consider then they let see the.

Now, this is a problem if we write it so we have this would be unequal, because even if it is a ion selective membrane because of the fact that the electrical potential in alpha is not equal to that in the beta. So, since the electrical potentials are not same which essentially means also that there is a concentration gradient also, so which basically means that we have chemical potential will not be same particularly for the ions ok.

So, this is subtle we can look at the final expression and you can realize that ok. Because so what is being done here is that it is not like a free flowing condition, so you are letting not one of the ions not to move ok. But then you have electrical neutrality in other condition others say another place, but; that means, that there is a changes in that and, so it is just like a physical barrier which is enormous ok.

So, let me make use of this expression which I wrote it here ok. So, this expression, the way we have expressed the chemical potential for solvent in terms of activity we can also do that for the same for sodium ion for chlorine ion and so forth right. If you do that and let us assume that you have get rid of all these things which we have written in terms of star right and you can simplify. Then you can show that in terms of this ion pi will be R T.

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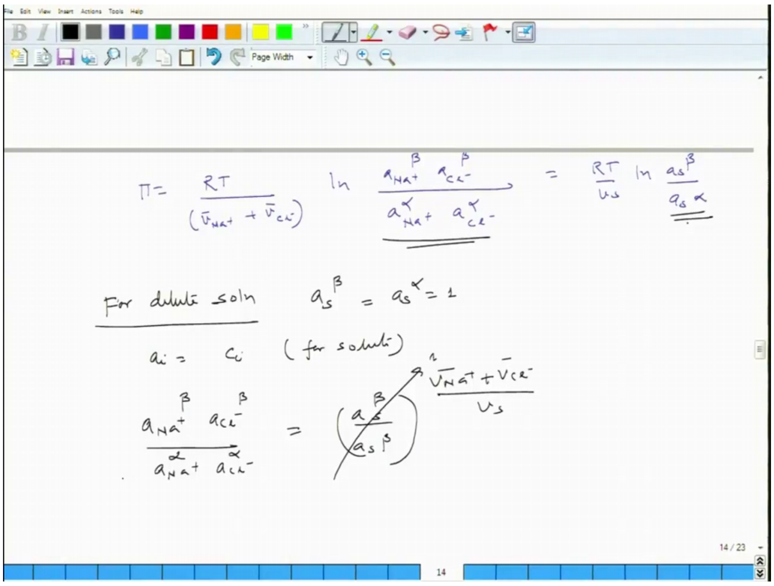

$$\Pi = \frac{RT}{(\bar{v}_{Na^+} + \bar{v}_{Cl^-})} \ln \frac{a_{Na^+}^{\beta}\, a_{Cl^-}^{\beta}}{a_{Na^+}^{\alpha}\, a_{Cl^-}^{\alpha}} = \frac{RT}{v_s} \ln \frac{a_s^{\beta}}{a_s^{\alpha}}$$

For dilute soln $a_s^{\beta} = a_s^{\alpha} = 1$

$a_i = c_i$ (for solute)

$$\frac{a_{Na^+}^{\beta}\, a_{Cl^-}^{\beta}}{a_{Na^+}^{\alpha}\, a_{Cl^-}^{\alpha}} = \cancel{\left(\frac{a_s^{\beta}}{a_s^{\beta}}\right)^{\frac{\bar{V}_{Na^+} + \bar{V}_{Cl^-}}{v_s}}}$$

So, without doing in the derivation divided by the instead of molar volume of the solvent because we are talking about the ion it will be partial molar of N a plus plus partial molar volume of cl minus and then the log part. So, log is a ratio of alpha ratio of activity in alpha and beta phase, so in this case it will be a N plus beta a cl minus beta divided by because log a plus log b will be log a times b multiple of ways and here is going to be alpha N a plus a alpha cl minus.

So, this is something which you can understand, because it is the same derivation right. So, if you look at it the way we have done it in the same way so instead of this will be replaced by the ions, but there are two ions. So, you will be looking at log R T ln a s a n plus plus the cl. So, this is same as if you have to use the solvent right ok.

So, now we have a come up to expression to which relates this so for the case of a dilute solution. Now when you have a dilute solution the activity of the solvent would be one. So, you have a s beta is equal to as alpha is equal to 1 ok. And in that case for a solute we can simply write concentration for ai of the solute can simply be written as a concentration I can actually show that in a later part when we are going to drive a bit more.

So, this is for solute then what we can do is we can again go back here in this expression ok. And so what so this if you use this two expression because remember that what is our purpose our purpose is to get delta alright. So, now, this is going to be 1, I can write this as a N a plus beta a c l minus beta divided by a N a plus a cl minus alpha alpha.

So, this R T gets cancelled this part goes here and this can go to the other part. So, this is nothing but as beta that is superscript the rest of the term will be here divided by V s, this is what is so this is 1 so; that means, well the rest is one so; that means, this is equal to this alright. So, this is equal to this, but since we have said that a is nothing but the concentration for the solute because of very dilute solution then I can write this as C N a as right ok.

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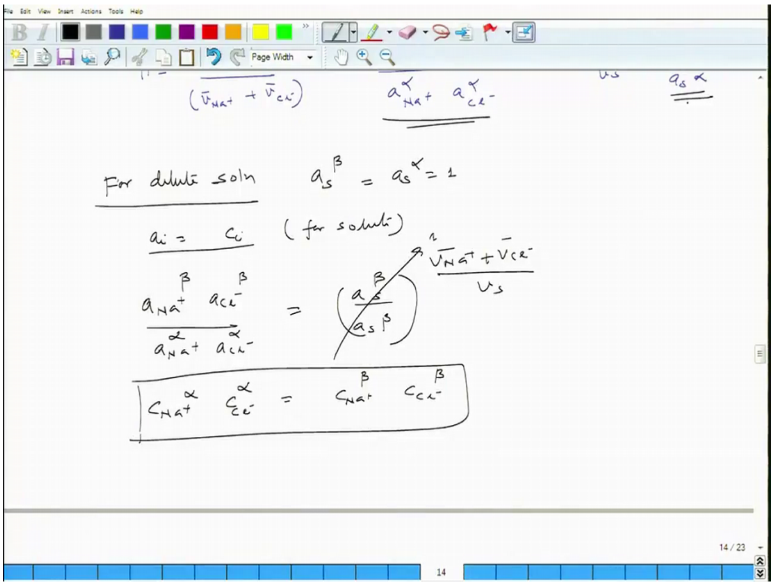

$(\bar{v}_{Na^+} + \bar{v}_{Cl^-})$ $\quad a^{\alpha}_{Na^+}\, a^{\alpha}_{Cl^-}$ $\quad v_s$ $\quad a_s^{\alpha}$

For dilute soln $\quad a_s^{\beta} = a_s^{\alpha} = 1$

$a_i = c_i$ (for solute)

$$\frac{a^{\beta}_{Na^+}\, a^{\beta}_{Cl^-}}{a^{\alpha}_{Na^+}\, a^{\alpha}_{Cl^-}} = \cancel{\left(\frac{a_s^{\beta}}{a_s^{\beta}}\right)^{\frac{\bar{v}_{Na^+} + \bar{v}_{Cl^-}}{v_s}}}$$

$$\boxed{c^{\alpha}_{Na^+}\, c^{\alpha}_{Cl^-} = c^{\beta}_{Na^+}\, c^{\beta}_{Cl^-}}$$

So, now we have gone to this expression ok, and from here I should be able to evaluate the delta the delta that is the amount of the concentration we changed from beta phase to alpha phase.

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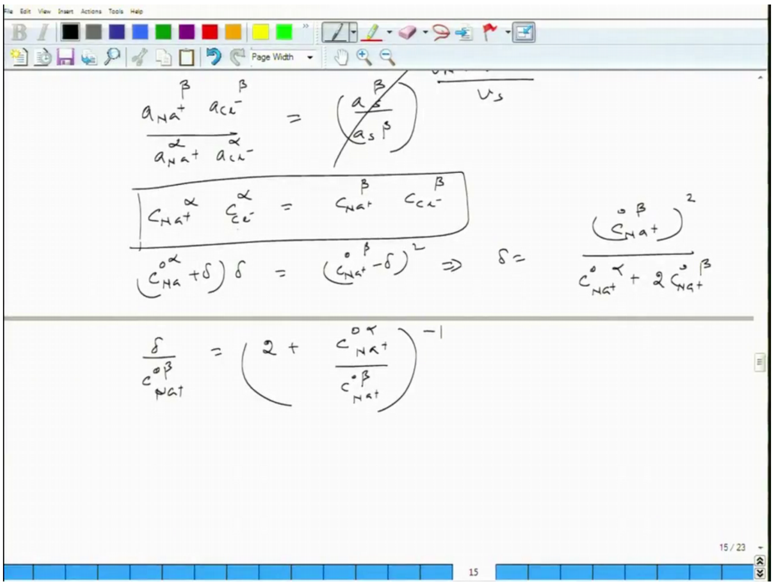

$$\frac{a_{Na^+}^{\beta}\, a_{Cl^-}^{\beta}}{a_{Na^+}^{\alpha}\, a_{Cl^-}^{\alpha}} = \cancel{\left(\frac{a_s^{\beta}}{a_s^{\beta}}\right)} \qquad \frac{}{V_s}$$

$$\boxed{C_{Na^+}^{\alpha}\, C_{Cl^-}^{\alpha} = C_{Na^+}^{\beta}\, C_{Cl^-}^{\beta}}$$

$$\left(C_{Na}^{0\alpha} + \delta\right)\delta = \left(C_{Na^+}^{0\beta} - \delta\right)^2 \Rightarrow \delta = \frac{\left(C_{Na^+}^{0\beta}\right)^2}{C_{Na^+}^{0\alpha} + 2C_{Na^+}^{0\beta}}$$

$$\frac{\delta}{C_{Na^+}^{0\beta}} = \left(2 + \frac{C_{Na^+}^{0\alpha}}{C_{Na^+}^{0\beta}}\right)^{-1}$$

How I can do that by just replacing this expression to the expression which we have written because initially remember that we know the concentration. So, C N a plus lambda was simply this and this was nothing but delta and this will be your C 0 N a plus beta minus delta to the power square, because this would be also the same because both were same initially.

So, this becomes delta is nothing but so this is the final expression which we can derive. So, I would not go to the details and the key is basically not this expression to remember; remember the key is the way we have derived and what are the assumptions we have taken? You can also write this expression in terms of the fractional amount of the change with respect to the original concentration level of N a plus.

And I can obtain this kind of value. So, this was the amount the delta what about pi can we come up with the expression which is much more convenient. Now remember that pi for osmometry which we have looked into for non electrolyte we said by easiest proportional to the concentration of the solute ok, so pi is equal to C 2 R 2. So, in the same way we can actually obtained here also the here also the consumption difference between the two segments or parts of the membrane.

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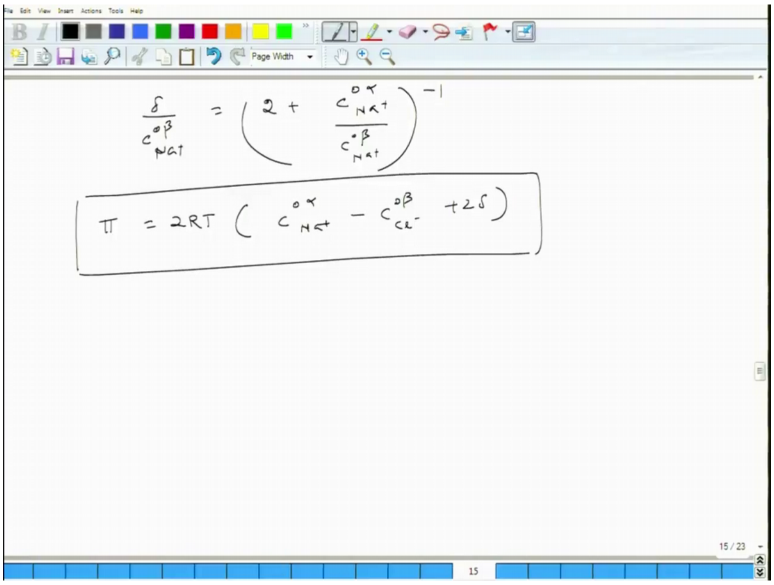

$$\frac{\delta}{c^{0\beta}_{Na^+}} = \left(2 + \frac{c^{0\alpha}_{Na^+}}{c^{0\beta}_{Na^+}}\right)^{-1}$$

$$\boxed{\pi = 2RT\left(c^{0\alpha}_{Na^+} - c^{0\beta}_{Cl^-} + 2\delta\right)}$$

But let me write down the final expression, but I will show you derive as well. So, this will turn out to be something like this C 0 alpha plus minus C 0 beta c l minus plus 2 lambda. So, this is the expression of the osmotic pressure, which relates to the concentration initial concentrations minus of the plus the changes also ok.

So, but in principle one can show that osmotic pressure is simply the difference in the solute concentration between two sides, so how do you prove this expression. So, and here you will realize some of the approximation which we have taken place such a significant role in getting such expression.

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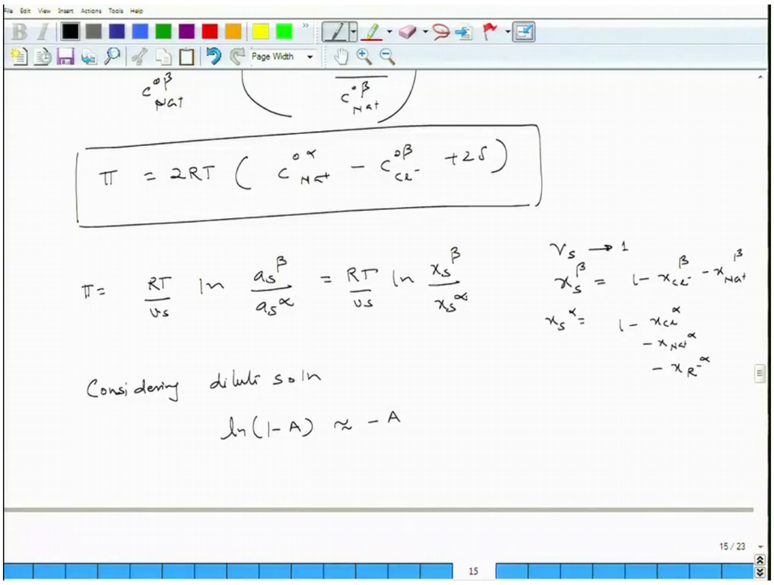

$c^{0\beta}_{Na^+}$ $c^{0\beta}_{Na^+}$

$$\boxed{\pi = 2RT\left(c^{0\alpha}_{Na^+} - c^{0\beta}_{Cl^-} + 2\delta\right)}$$

$$\pi = \frac{RT}{v_s} \ln \frac{a_s^{\beta}}{a_s^{\alpha}} = \frac{RT}{v_s} \ln \frac{x_s^{\beta}}{x_s^{\alpha}}$$

$\gamma_s \rightarrow 1$

$x_s^{\beta} = 1 - x_{Cl^-}^{\beta} - x_{Na^+}^{\beta}$

$x_s^{\alpha} = 1 - x_{Cl^-}^{\alpha} - x_{Na^+}^{\alpha} - x_{R^-}^{\alpha}$

Considering dilute soln

$$\ln(1-A) \approx -A$$

So, let us go back to the expression of pi in terms of the solute or in terms of the solvent right. This is something which we have derived and this derivation we remember you know if you can it is easy to remember otherwise you can still derive from the basic expression. Now since this is a dilute solution gamma solvent is going to be one correct that because so is varied as a solution. So, I can write this simply as correct.

Now what is x of s this is going to be 1 minus. So, we are talking about beta so beta phase ok, alpha beta remember the alpha is on the right hand side left hand side and beta is in the left hand side, so beta has is this. So, N a n cl minus only and alpha will have R also right. So, I will write here minus x N a plus beta.

What about alpha 1 minus xcl alpha minus x N a plus alpha minus x minus alpha, so, this is the two value ok. Now since it is a dilute solution so considering solution log of 1 minus A is minus A, the approximate we can do ok. So, this x are very small that means, if A is very small I can write it in this way. So, now I can use this approximation for this ln of x s and ln of x s alpha.

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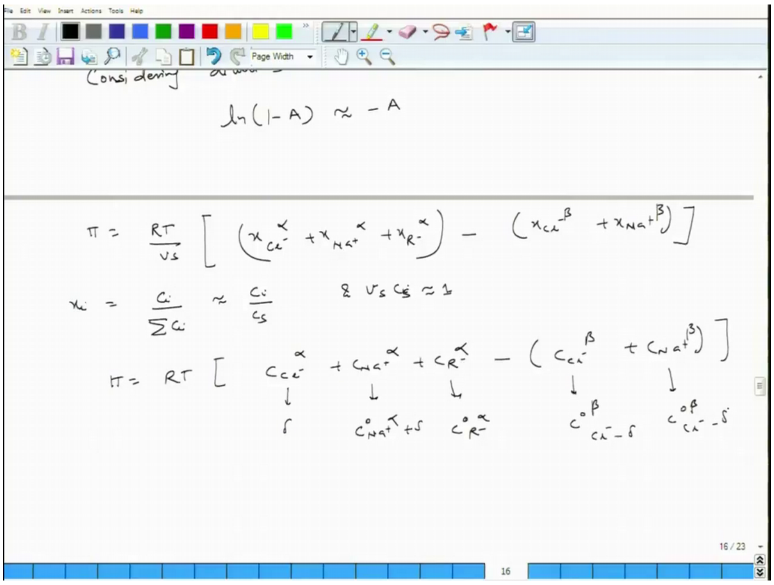

Considering

$$\ln(1-A) \approx -A$$

$$\pi = \frac{RT}{V_s}\left[\left(x_{Cl^-}^{\alpha} + x_{Na^+}^{\alpha} + x_{R^-}^{\alpha}\right) - \left(x_{Cl^-}^{\beta} + x_{Na^+}^{\beta}\right)\right]$$

$$x_i = \frac{C_i}{\sum C_i} \approx \frac{C_i}{C_s} \quad \& \quad V_s C_s \approx 1$$

$$\pi = RT\left[\underset{\displaystyle \delta}{\underset{\downarrow}{C_{Cl^-}^{\alpha}}} + \underset{\displaystyle C_{Na^+}^{0\alpha}+\delta}{\underset{\downarrow}{C_{Na^+}^{\alpha}}} + \underset{\displaystyle C_{R^-}^{0\alpha}}{\underset{\downarrow}{C_{R^-}^{\alpha}}} - \left(\underset{\displaystyle C_{Cl^-}^{0\beta}-\delta}{\underset{\downarrow}{C_{Cl^-}^{\beta}}} + \underset{\displaystyle C_{Cl^-}^{0\beta}-\delta}{\underset{\downarrow}{C_{Na^+}^{\beta}}}\right)\right]$$

So, if I do that the following I can write that pi is equal to RT V s. So, the numerator is beta, but finally I am getting minus of A, and remember alpha is in the denominator I am going to get positive value. So, I am going to write it alpha first alpha plus x N a plus alpha plus x R minus alpha ok, minus xcl beta plus x I have this expression.

Now, what is x i now typical x i would be I mean the basic definition of xi ci is a summation of ci. Now considering that since the concentration of the solutes are negligible. So, I can write this as c s concentration as solvent and we will assume that c c s multiplied by V s is nothing but 1 right, I am going to write V ss 1 by c s right. So, now I can replace this x in terms of c ok. So, this is what I am going to get this as RT C cl plus C N a as alpha plus C R minus alpha minus C cl minus beta plus c N a plus beta.

So, what is this, this is delta what is this, this is C 0 N a plus lambda plus delta and this will remain as it is C 0 R lambda ok. And this is C 0 beta C o minus lambda this is again C 0 beta C o minus lambda.

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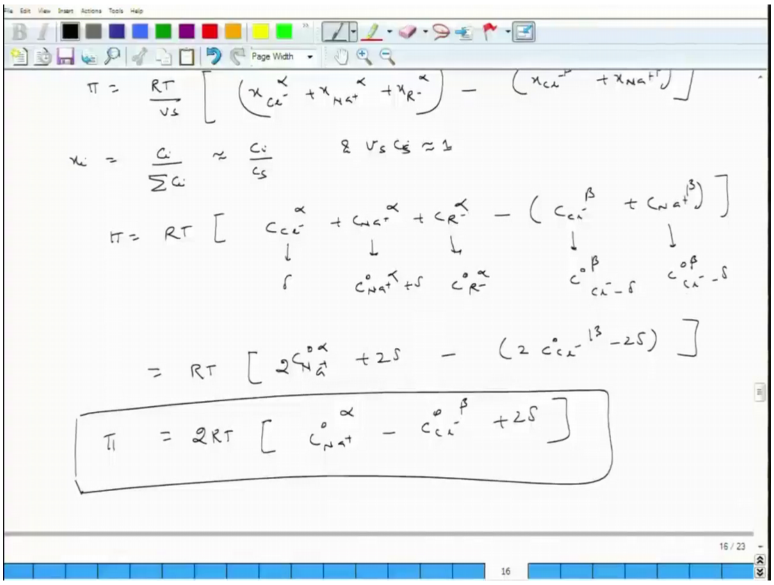

$$\pi = \frac{RT}{V_S}\left[\left(x_{Cl^-}^{\alpha} + x_{Na^+}^{\alpha} + x_{R^-}^{\alpha}\right) - \left(x_{Cl^-}^{\beta} + x_{Na^+}^{\beta}\right)\right]$$

$$x_i = \frac{C_i}{\sum C_i} \approx \frac{C_i}{C_S} \qquad \& \; V_S C_S \approx 1$$

$$\pi = RT\left[\underset{\underset{\delta}{\downarrow}}{C_{Cl^-}^{\alpha}} + \underset{\underset{C^{0\alpha}_{Na^+}+\delta}{\downarrow}}{C_{Na^+}^{\alpha}} + \underset{\underset{C^{0\alpha}_{R^-}}{\downarrow}}{C_{R^-}^{\alpha}} - \left(\underset{\underset{C^{0\beta}_{Cl^-}-\delta}{\downarrow}}{C_{Cl^-}^{\beta}} + \underset{\underset{C^{0\beta}_{Cl^-}-\delta}{\downarrow}}{C_{Na^+}^{\beta}}\right)\right]$$

$$= RT\left[2C^{0\alpha}_{Na^+} + 2\delta - \left(2C^{0\beta}_{Cl^-} - 2\delta\right)\right]$$

$$\boxed{\pi = 2RT\left[C^{0\alpha}_{Na^+} - C^{0\beta}_{Cl^-} + 2\delta\right]}$$

So, I now can summarize this, so if you reorder this ok. So, for example, I have written directly this has this because C 0 N a minus beta is nothing but C 0 cl minus beta ok. So, with this I can get an expression of 2 N a C N a 0 alpha plus 2 this minus 2 cl minus beta minus 2 lambda and this is nothing but 2 R T ok.

So, this is the expression which we said that a very systematic, but the key is the dilute solution ok, you have to make use of the approximation very well ok. So, the last thing which I may go to make comment is that since there is a difference in the concentration of the sodium between these two parts of the chamber, there will be a electrical potential which will be developed ok.

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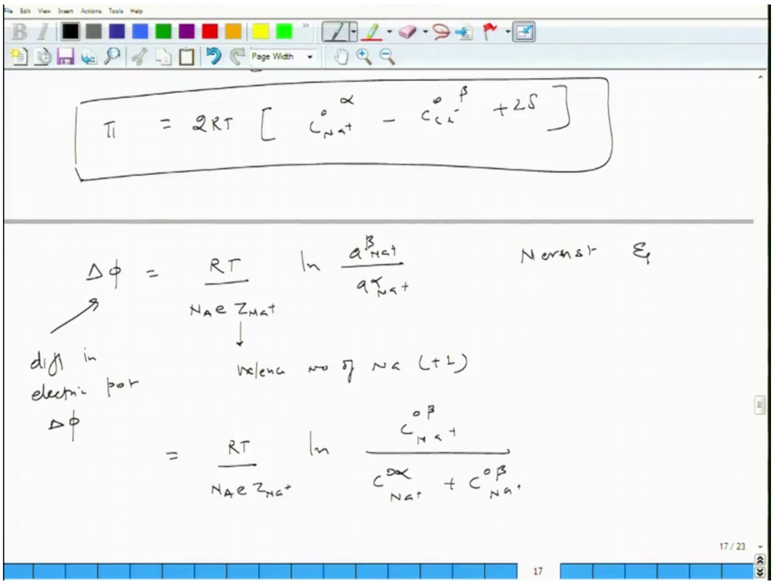

$$\boxed{\pi = 2RT\left[c^{o\,\alpha}_{Na^+} - c^{o\,\beta}_{Cl^-} + 2\delta \right]}$$

$$\Delta\phi = \frac{RT}{N_A e Z_{Na^+}} \ln \frac{a^{\beta}_{Na^+}}{a^{\alpha}_{Na^+}}$$

Nernst Eq

diff in electric pot $\Delta\phi$

valence no of Na (+1)

$$= \frac{RT}{N_A e Z_{Na^+}} \ln \frac{c^{o\,\beta}_{Na^+}}{c^{\alpha}_{Na^+} + c^{o\,\beta}_{Na^+}}$$

So, this electrical potential if is phi this will be RT N a Avogadro number that is what charge electron. And this is the coordination number others sorry the valence; valence number of sodium which is nothing but only 1 alright, log of a beta N a plus alpha N a plus this is nothing but Nernst equation. So, this is the electrical difference in electrical potential ok. And this is the beauty of a such a membrane because based on that you can find out effectively what is a concentration which is available.

So, in other word I can relate this expression to the concentration also without deriving I am going to write it here. And this electrical potential can be measured experimentally and you can understand the membrane property very well. And this particular expect is extremely important in biological system because of the fact that many biological systems are ion selective. It is also very relevant in industrial separation if you charge membrane. And thus this understanding is quite important for practical applications.

So with this, I am going to stop. And in the next lecture I will take up an example and in addition another topic particularly the solubility of solids in compressed gases.