BioMEMS and Microfluidics
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Lecture- 09, 10

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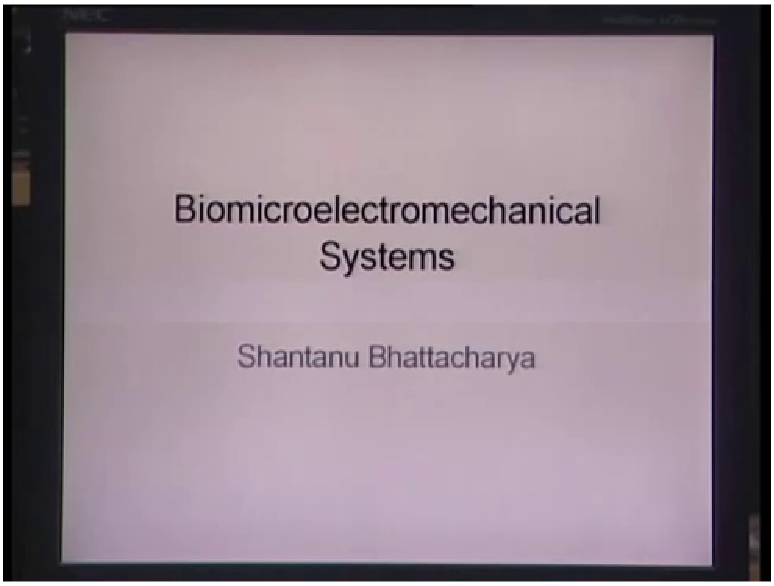

Biomicroelectromechanical Systems

Shantanu Bhattacharya

So, welcome back. I just to review what a we were talking in the last lecture; we try to generate an equation where in the free energy per mole of the system, which is also expressed as a K T ln gamma i. Gamma i being activity coefficient was equated to the total amount of work that was needed to bring a charge Zie into the you know minus Zie into the central ion of interest which is a plus Zie charge. In other words in order to give a charge it is counter ionic cloud the amount of work which is done, is given by you know this integral of dw. So, from the equation we try to get an expression in terms of gamma i as is the following.

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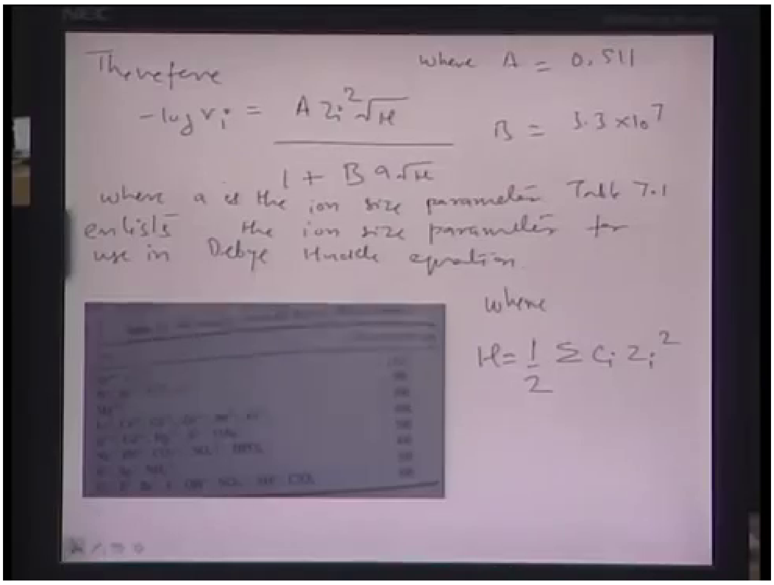

Therefore

$$-\log \gamma_i = \frac{A Z_i^2 \sqrt{\mu}}{1 + B a \sqrt{\mu}}$$

where A = 0.511

$B = 3.3 \times 10^7$

where a is the ion size parameter Table 7.1 enlists the ion size parameter for use in Debye Huckle equation

where

$$\mu = \frac{1}{2} \sum C_i Z_i^2$$

$$-\log \gamma_i = \frac{A Z_i^2 \sqrt{\mu}}{1 + B a \sqrt{\mu}}$$

$$\mu = \frac{1}{2} C_i Z_i^2$$

So, ln gamma i, excuse me.

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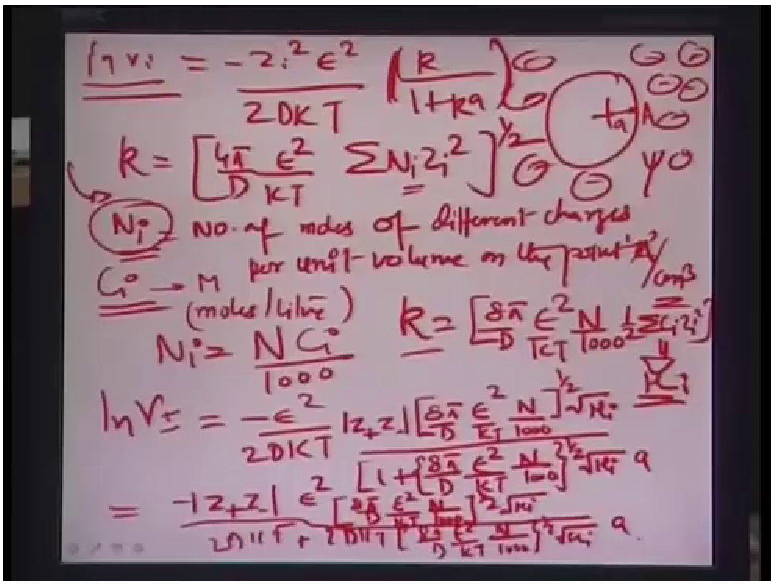

$$\ln \gamma_i = \frac{-Z_i^2 \epsilon^2}{2DKT} \left(\frac{\kappa}{1 + \kappa a} \right)$$

$$\kappa = \left[\frac{4\pi}{D} \frac{\epsilon^2}{KT} \sum N_i Z_i^2 \right]^{1/2}$$

N_i → No. of moles of different charges per unit volume on the solution/cm^3

C_i → M (moles/litre)

$$N_i = \frac{N C_i}{1000}$$

$$\kappa = \left[\frac{8\pi}{D} \frac{\epsilon^2}{KT} \frac{N}{1000} \frac{1}{2} \sum C_i Z_i^2 \right]$$

$$\ln \gamma_\pm = \frac{-\epsilon^2}{2DKT} \frac{|Z_+ Z_-| \left[\frac{8\pi}{D} \frac{\epsilon^2}{KT} \frac{N}{1000} \right]^{1/2} \sqrt{\mu_i}}{\left[1 + \left\{ \frac{8\pi}{D} \frac{\epsilon^2}{KT} \frac{N}{1000} \right\}^{1/2} \sqrt{\mu_i}\, a \right]}$$

$$= \frac{-|Z_+ Z_-| \epsilon^2 \left[\frac{8\pi}{D} \frac{\epsilon^2}{KT} \frac{N}{1000} \right]^{1/2} \sqrt{\mu_i}}{2DKT + 2DKT \left[\frac{8\pi}{D} \frac{\epsilon^2}{KT} \frac{N}{1000} \right]^{1/2} \sqrt{\mu_i}\, a}$$

Natural log of gamma *i* the activity coefficient also came equivalent to

$\ln\gamma_i = \frac{-Z_i^2 \in^2}{2DKT}\left(\frac{k}{1+ka}\right)$. *a* here was the ion size parameter, it is an indication of tentatively what is the size of the central ion of interest. So, also we know that you know k essentially is nothing but $k = \left[\frac{4\pi}{D}\frac{\in^2}{KT}\sum N_i Z_i^2\right]^{1/2}$. In other words we can express this in the more appropriate manner by assuming that what is really N_i ? N_i is essentially the number of moles of different chargers whether it is positive or negative different charges. We remember the way we talked about the subscript i in our lectures before. Per unit volume, per unit volume on the point A. We were talking about a central ion in a point A which was closed by where the potential was phi and then you know negative ion atmosphere which was all the way around just for recapitulating what we have done earlier. So, this was the point A essentially, was the point A and which was the distance of small *a* from the center of this charge. This was the point A, the radius here is small *a*.

So, we can really express this in terms of the concentration of the various ions that are there in the solution and from which we formulated the mean concentration. So, what we try to estimate this as a since Ci is also in terms of mole, molar or moles per liter and this Ni was per centimeter cube, because you know it was all CGS units which we were used at the beginning of the 19th century to explain at least problems majority of the problems in main this chemistry or related to charge essentially in chemistry. So, here we could consider you know the number of moles per unit volume N_i to the product of the Avogadro number N, which 6.023×10^{23} the numbers and 1 mole divided into the concentration Ci by 1000; 1000 cc or 1000 centimeter cube makes 1 litter. $N_i = \frac{NC_i}{1000}$.

So, from these 2 of from this kind of an expression in the $k = \left[\frac{8\pi}{D}\frac{\in^2}{KT}\frac{N}{1000}\frac{1}{2}\sum C_i Z_i^2\right]^{1/2}$. And this is nothing but the mean ion concentration of i, so it can call it mu i. So, we today try to go ahead then this and try to find out what this ln gamma i would been terms of this final and full expression for K. And we get the 10 ln gamma i and now i would like to change this subscript i by it is a sense you know the way that we had start at all these things we had assume i could be either positive or could be negative. So, i write gamma plus, a plus minus here is equal to $\overset{-}{+Z_{\square}}$ $Z_{\square}$ $\ln \gamma_i \pm = \frac{-\in^2}{2\,DKT}$. So, for the principle of electro neutrality you know the positive and negative charges and otherwise electric neutral medium would be equal exactly opposite.

So, even if we, do the total amount of positive and total amount of negative charge that would be same as reporting the square of the magnitude the charge, of course today the magnitude of Z plus Z minus times of k by 1 plus ka. $\overset{-}{+Z_{\square}}$ $Z_{\square}\frac{k}{1+ka}$ $\ln \gamma_i \pm = \frac{-\in^2}{2\,DKT}$ And k here comes out to be equal to 8 pi; let me just go ahead in shift this down a little bit. So, that it will be convenient. So, this is Z plus Z minus mod of times k which is 8 pi by D, right epsilon square by KT, N by 1000 times of this is whole half of course, times of root of mu i divided by 1 plus; the value of K again being 8 pi by D epsilon square by KT, N by 1000 whole half, Second bracket sorry. Whole half times of root mu i times of a, where a is the ion size parameter.

$$\overset{-}{+Z_{\square}}$$

$$Z_{\square}\frac{\left[\frac{8\pi}{D}\frac{\in^2}{KT}\frac{N}{1000}\right]^{1/2}\sqrt{\mu_i}}{1+\left[\frac{8\pi}{D}\frac{\in^2}{KT}\frac{N}{1000}\right]^{1/2}\sqrt{\mu_i}\,a}$$

$$\ln \gamma_i \pm = \frac{-\in^2}{2\,DKT}$$

And this gives us very interesting you know way of a presentation. We could couple this all together and you know just write it as in the following manner. Z plus Z minus of course, modulus and epsilon square is taken here writing the value of 8 pi by D epsilon square by KT, N by 1000 half root mu i, right and on the denominator you have twice DKT plus twice D KT times of 8 pi by D, E square by KT, N by 1000 whole half root of mu i times of a. In other words, so therefore, we can write this expression as in a little different manner, so there it can be more simplified.

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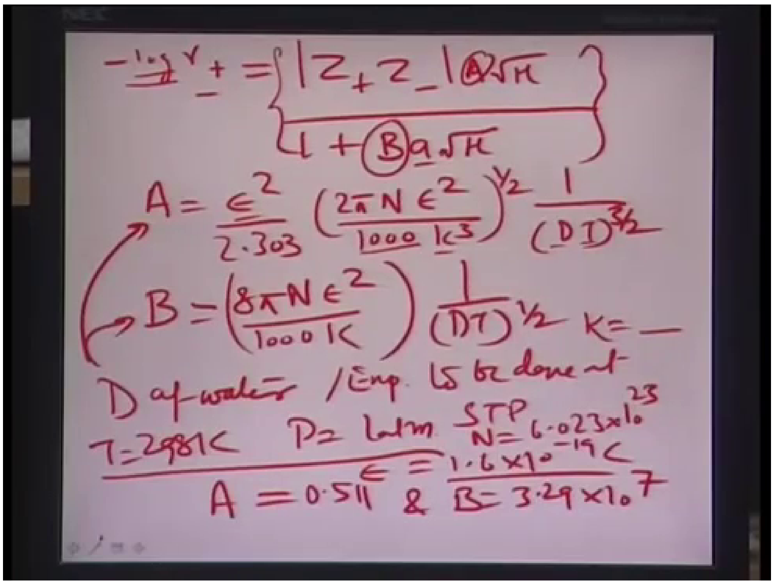

$$-\log\gamma_{\pm} = \left\{\frac{|Z_+Z_-| A\sqrt{\mu}}{1+Ba\sqrt{\mu}}\right\}$$

$$A = \frac{\epsilon^2}{2.303}\left(\frac{2\pi N\epsilon^2}{1000\,k^3}\right)^{1/2}\frac{1}{(DT)^{3/2}}$$

$$B = \left(\frac{8\pi N\epsilon^2}{1000\,K}\right)\frac{1}{(DT)^{1/2}} \quad k = \_\_$$

D of water / temp. is to be done at

$T = 298K$ $P = 1atm$ STP $N = 6.023\times10^{23}$

$\epsilon = 1.6\times10^{-19}C$

$A = 0.511$ & $B = 3.29\times10^{7}$

¿

−

$+Z_{\square}$

$Z_{\square} A\sqrt{\mu}$

¿

$-log\gamma_i \pm =$ ¿

$$A = \frac{\epsilon^2}{2.303}\left(\frac{2\pi N\epsilon^2}{1000\,k^3}\right)^{1/2}\frac{1}{(DT)^{3/2}}$$

$$B = \left(\frac{8\pi N\epsilon^2}{1000\,K}\right)\frac{1}{(DT)^{1/2}}$$

So, you have minus log of gamma plus minus alright. And you can write this as Z plus Z minus A times of the root mu divided by 1 plus B times of. So, therefore, this can be represented as a 1 plus B times of a times of root of mu. This A's and B's are just you know it is like for convenience. So, overall convenience we can report these and if you really where represent the whole thing in terms of A mind you know there is a log here which is equal to 2.303 ln. So, 1 by 2.303 ln value. So, essentially A here is nothing but square of E by 2.303 ; and I am juts simplifying and writing down which is convenient 2 pi N epsilon square by 1000 k 3. This is just by simplification that you can very present this particular form with 1 plus B times a root mu here, Zi square times of a times root of mu. Zi square is again modulus of Z plus into Z minus right, times.

So, this raise to the power of, this raise of half times of 1 by DT to the power of 3by 2. That is how the A can be represented and the B here in this equation can be represented as 8 pi N epsilon square by 1000 k times of 1 plus DT to the power half. Interestingly if we put the values of the dielectric constant of water in most of the cases the solutions which are be investigated it is essentially an aqueous base solution of designs. So, the basic medium there is what are the basic dielectric is water. So, if we consider put the value of the dielectric constant D of water. In these expressions A and B simultaneously and consider the experiment to be done at STP, experiment to be done at Standard Temperature Pressure you know. So, 298 Kelvin, 1 atmosphere pressure this kind of a convention this type of condition and then of course, N's value is a new fixed value 6.023×10^{23} numbers of atoms or molecules or charges in this case, excuse me.

So, therefore, we can calculate the values of A and B, if you look at an also, also the E here as 1.6×10^{-19}, coulomb charges of electron. So, the A it kind of emphasis all these constant values you have k value for the Boltzmann constant, you put the Boltzmann constant value: you have 1000, N, you have a E square and you have dielectric constant for water and temperature 298 Kelvin. So, you can compute all these values and it is comes out to be 0 .511 and B comes out to be 3.29×10^{7} respectively very large value. But the very fact is that because this B is also in product with the ion size parameter which may be a few nanometers and will be investigating and estimating few tables later on for the ion size parameter A. So, therefore, the equation in the gamma value would hold consistency.

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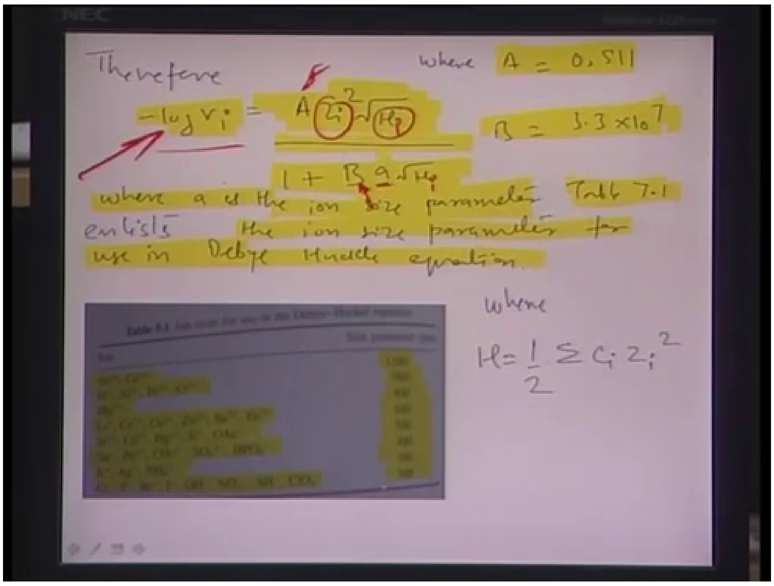

Therefore

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{\mu_i}}{1 + B a \sqrt{\mu_i}}$$

where $A = 0.511$

$B = 3.3 \times 10^{7}$

where a is the ion size parameter Table 7.1 enlists the ion size parameters for use in Debye Huckel equation.

where

$\mu = \frac{1}{2} \sum c_i z_i^2$

Therefore, the whole equation can really written down in the terms of minus log gamma i is seen here, equals $\begin{array}{c} \text{¿} \\ - \\ +Z_{\square} \\ Z_{\square}\, A\sqrt{\mu} \\ \text{¿} \\ -l\,og\gamma_i \pm = \text{¿} \end{array}$, where A is calculated to be 0.511. B is calculated to be 3.3×10^{7} by assuming STP: Standard Temperature Pressure; and the various parametric values for N Avogadro number epsilon electronic charge so and so forth. So, the A is very interesting proposition here, the A here you see in this particular area here, the A is the ion size parameter. So, it can be very well enlisted and some standard ion size parameters are listed here if you can see here you know selenium ions or thin ions of quarter balance state is an ion size parameter of about approximately 1100 picometer. Similarly you have you know the H plus l plus 3 Fe^{3+} and Cr minus these values they have about 900 picometers. And so essentially these all ion size parameters have been investigated, evaluated from the Debye-Huckle theory. And they are tabulated and they are used often none for all sort of experiments.

So therefore, all the equation, all the parameters in this particular equation here for estimating the activity coefficient exist; you know what Z i square is you can calculate, what the mu i, is the activity coefficient of the you know of the mean concentration of the particular solution is. You know what A and B are, these are constants which are estimated by this Standard TP; STP conditions: Standard Temperature Pressure conditions, and therefore ion size parameter if we borrow it from this stable which has been probably estimated by experiments can be used very well to calculate what is the activity of a particular ion of interest while you are doing the deduction protocol.

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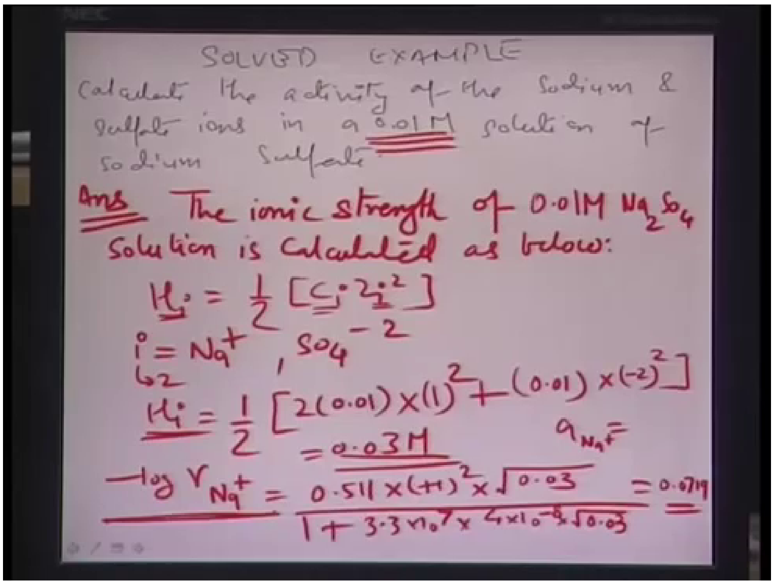

SOLVED EXAMPLE

Calculate the activity of the sodium & sulfate ions in a 0.01 M solution of sodium sulfate

Ans The ionic strength of 0.01M Na_2SO_4 solution is calculated as below:

$\mu_i = \frac{1}{2}[C_i Z_i^2]$

$i = Na^+, SO_4^{-2}$

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$\mu_i = \frac{1}{2}[2(0.01)\times(1)^2 + (0.01)\times(-2)^2]$

$= 0.03 M$

$a_{Na^+} =$

$-\log \gamma_{Na^+} = \frac{0.511\times(+1)^2\times\sqrt{0.03}}{1+3.3\times10^7\times4\times10^{-8}\sqrt{0.03}} = 0.0719 =$

$$\mu_i = \frac{1}{2} C_i Z_i^2$$

Having set that, let us actually look into and little bit of you know kind of a solved example. Where we talk about how to calculate the activity of sodium and sulfate ions independently in a let say 0.01 molar solution of sodium sulfate. So, you have a case where you have a sodium sulfate solution and you would like to find out the activity coefficient of sodium and sulfate ions independently or individually by looking at you know the Debye-Huckle set of equations.

So, let us try to solve this, we have a case where need to find out the activity given of the ionic strength of or given the molarity of the sudden sulfate solutions. So, the ionic strength of the sodium sulfate of the 0.01 molar Na_2So_4 sodium sulfate. Solution is calculated as below: you have a half Ci Zi square molarity. How many i’s are there? The there is Na plus and there is a SO_4 minus 2. So, there are two i's. So, mu i in this case would be half of concentration of Na plus which is essentially 0.02 molar. So, 2 into 0 .01. Is the sodium sulfate solution is a molarity mind you of 0.01. So, there are 2 sodium ions every molecule of Na_2So_4; and so therefore, you have the overall molarity of a Na plus as 0.02 molar. So, the concentration times of the square on the valency which is plus 1 in case of sodium. Plus and this is essentially a summation term because it is a cumulative all the positive and negative charges.

So, now, you have the concentration for SO_4, which is on the 1 molar or which is only 1 in molecule. So, you have a concentration of 0. 01 molar times off, now the charge here is minus 2. Because of so for or sulfate ion evaluate valiant ion essentially, square of that. So, this comes out to be from calculations equal to 0.03 molar.

$$\mu_i=\frac{1}{2}\left[2(0.01)\times 1^2+(0.01)\times(-2)^2\right]=0.03\,M$$

So, this is the mean ionic strength this sodium sulfate solution. So, once the mean ionic strength is calculated. So, the things are easy you just need to calculate minus log of gamma N a plus in this case which should be equal to let say you know the 0.511. The A term terms of times of square on the valency on the sodium which is a plus 1 square times of root over mu i, where mu i is 0.03 molar and divided by 1 plus B which in this case is 3.3 into 10 to the power of 7 times of the ion size parameter of Na plus; which can be obtain from the table as given before here, that the sodium Na plus essentially if you look at this particular zone here as an ion size parameter about 400 picometers. Or 4 into 10 to the power of minus 10 meters or a 4 into 10 to the power of minus 8 centimeters.

So, since we are actually using the CGS units for calculating everything here you would take the ion size parameter a as 4 into 10 to the power of minus 8 centimeters times of root of 0.03 molar. So, this comes out to be equal to 0.0719,

$$Na^{+\text{¿}}=\frac{0.511\times(+1)^2\times\sqrt{0.03}}{1+3.3\times10^7\times4\times10^{-8}\times\sqrt{0.03}}=0.0719$$

$$\gamma_{\text{¿}}-\log$$

that is what the ionic strength of the log of negative log of the ionic activity of Na plus is. So, let us calculate the do the same kind of calculation for the SO_4 ion.

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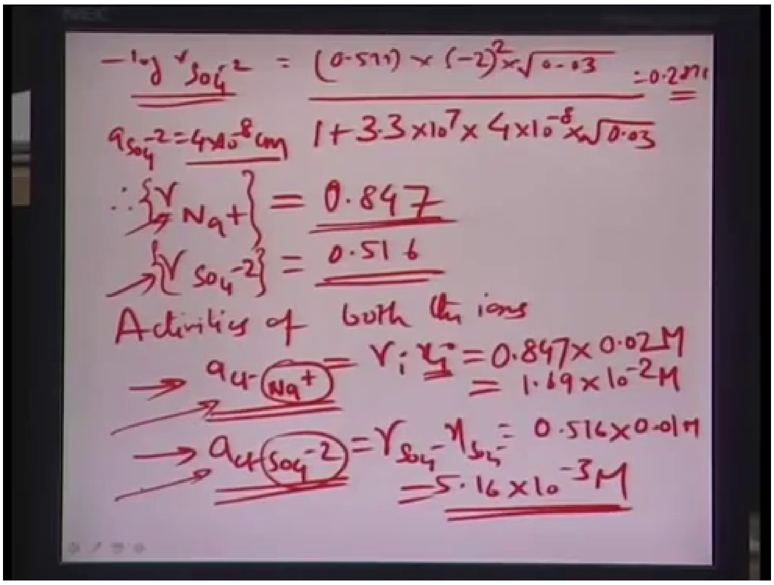

$$-\log \gamma_{SO_4^{2}} = \frac{(0.511) \times (-2)^2 \times \sqrt{0.03}}{1+3.3\times10^{7}\times 4\times10^{-8}\times\sqrt{0.03}} = 0.2876$$

$a_{SO_4^{-2}} = 4\times10^{-8}$ cm

$\therefore \gamma_{Na^+} = 0.847$

$\gamma_{SO_4^{-2}} = 0.516$

Activity of both the ions

$\rightarrow a_{ct}(Na^+) = \gamma_i\, \eta_i = 0.847 \times 0.02M = 1.69\times10^{-2}M$

$\rightarrow a_{ct}(SO_4^{-2}) = \gamma_{SO_4^-}\, \eta_{SO_4^-} = 0.516 \times 0.01M = 5.16\times10^{-3}M$

So, in case of SO4the activity can be the equation can be written is minus log gamma SO4 minus 2 equal to 0 .511 that is the a parameter a aspect the coefficient a times of square on the valency of sulfate then sulfates valency is minus 2. So, square on minus 2 times of root over 0.03 molar divided by 1 plus the B constant which is 3.3, 10 to be power seven times of the radius of SO4ion; which again through this particular figure here. So, SO_4^{-2} and Na plus are more or less in the same size domain this about 400 picometers.

So, essentially means the ion size parameters *a* for SO_4^{-2} should be about 4, 10 to the power minus 8 centimeter as before. Mind you again this, all these equations are in terms of CGS units. So, apart from the molarity which is standard universal unit the other equations, other components of the equation has essentially CGS corresponding units: Centimeter Gram Second unit. So, this comes out to be 4, 10 to the power minus 8 times of root of 2 times 0 point 03. And essentially that is calculated to be 0.2876.

$$-\log\gamma_{SO_4^{-2}} = \frac{0.511\times(-2)^2\times\sqrt{0.03}}{1+3.3\times10^{7}\times4\times10^{-8}\times\sqrt{0.03}} = 0.2876$$

So, taking anti logs on the both equations solved earlier, the activity of the sodium ion comes out to be 0.847 $\gamma_{Na^{+}} = 0.847$ and the activity of the sulfate ions of SO_4^{-2} in this case comes out to be 0.516. So, if we look at the craft, sorry these are the activity coefficients. Let me just rewrite the activity coefficient of the sodium ion comes out to be 0.847 and the activity coefficient of the SO4ion comes out to be 0.516. $\gamma_{SO_4^{-2}} = 0.516$

Now, if you want to look at really the activities of both the ions, which is also known as a Na plus; and this a is probably the activity do not confuse with it the ion size parameter. Let just turn, let just get a different name here for convenience say. Let say we have just write act instead of or act. Act Na plus equals gamma i times of x i is you know, x i is the ionic concentration of the particular analyte. So, in case of sodium you have 0.847 as the gamma i and the x i as you know in this case, you have 2 atoms per molecule and the overall concentration is 0 point 01. So, for sodium in the concentration is point 02 molars. So, in the activity in this case, is only about 1.69, 10 to the power of minus 2 molar.

$$+¿=\gamma_i \times x_i = 0.847 \times 0.02\,M = 1.69 \times 10^{-2}\,M$$

$$Na^{¿}\,act_{□}$$

And in case of $SO_4$the activity SO_4^{-2} can be the gamma SO_4^{-2} times of concentration of SO_4^{-2} , which is 0.516 above times of 0.01 molar mind you in 1 molecule. There is only one SO_4atom which is present; so therefore, it is concentration is only same as add of the Na_2SO_4solution.

$$act_{SO_4^{-2}} = \gamma_{SO_4^{-2}} \times x_{SO_4^{-2}} = 0.516 \times 0.01\,M = 5.16 \times 10^{-3}\,M$$

So, this comes out to be equal to 5.16, 10 to the power of minus 3 molar alright. So, that is how you are able to calculate the activity of Na plus and $\overset{-}{SO_4}□$ in a solution in a sodium sulfate solution by looking at the various aspects. Now what you would be, I would be interested to look at here is, that if you may just see the activities of both are different. So therefore, N a plus is a more active ion than SO_4minus. So, in such kind of situations there is a presence of both ions that is Na plus SO_4minus that is the tendency of the electrode to be heavily interfered by the Na plus ion if you are detecting, sulfate ions. So, you have to be careful in order to create a situation where the Na plus ion is blocked in a manner. So, that is activity is also blocked and the ion selective electrode only specifically pick up a SO_4minus ion in the presence of Na plus ion. Minus 2 ion in case of, SO_4^{-2} ion in place of or in the presence of Na plus ion.

So, you have a fairly good idea about activity coefficients at this time and how they would be calculated. So, once we are actually done with this activity coefficients, what is very important to find out here is that you know, due to this activities what is really the change in the EMF. The measured potential of such a solution where you have about more than one species of ions with interfering ions as well as the primary ion of interest. So, the essentially the E value, the potential value would change because of this participating other kind of interfering kind of ions and there is a set of equations called Nikolsky-Eisenman equation which is used for a predicting the EMF value of j such components together in you know in a solution in electro chemical solutions and to the effects of those components on the measured EMF of such a solutions.

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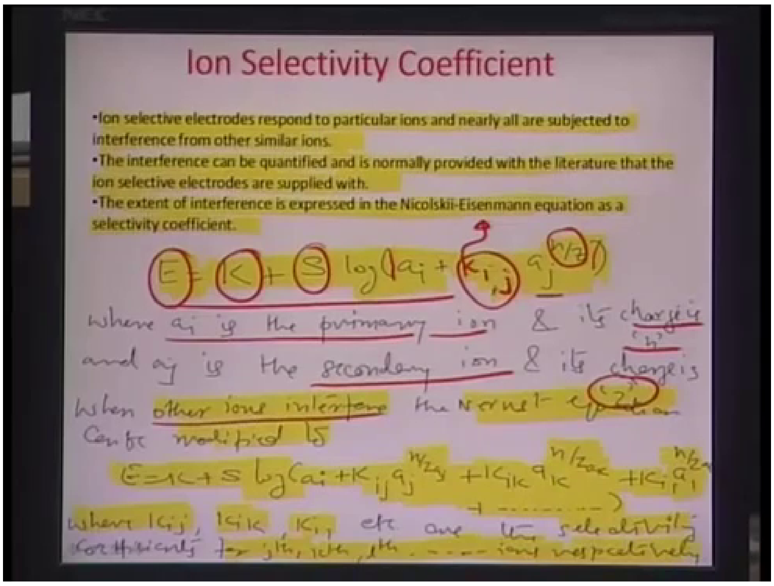

Ion Selectivity Coefficient

- Ion selective electrodes respond to particular ions and nearly all are subjected to interference from other similar ions.
- The interference can be quantified and is normally provided with the literature that the ion selective electrodes are supplied with.
- The extent of interference is expressed in the Nicolskii-Eisenmann equation as a selectivity coefficient.

$$E = K + S \log(a_i + K_{i,j} a_j^{n/z})$$

where a_i is the primary ion & its charge is 'n'
and a_j is the secondary ion & its charge is 'z'
When other ions interfere the Nernst equation can be modified as

$$E = K + S \log(a_i + K_{ij} a_j^{n/z_j} + K_{ik} a_k^{n/z_k} + K_{il} a_l^{n/z_l} + \dots\dots)$$

where K_{ij}, K_{ik}, K_{il} etc. are the selectivity coefficients for jth, kth, lth ...... ions respectively

So, for designing ion selective electrodes the very important factor is the ion selective ion selectivity coefficient. So, it is kind of quantification with the interference. So, in a nutshell we can summarize all these as that ion selective electrodes respond to particular ions and nearly all are subjected to interference from other similar ions. And the interference can be quantified is normally provided with the literature that ion selective electrodes supplied with. And the extend of interference is express by this set of equation Nikolsky-Eisenman equation was a selectively coefficient.

So, the EMF of given out by such a solution which has more than 1 ion of you know participating ions with one of interest the remaining interfere ions, can be also written as K plus S log of ai which is the activity of the primary ion of interest plus K ij and this is called the ion selectivity coefficient, this is a measured quantity. And I demonstrating, I will be just showing a table we should be talking about several such values of K ij, which means that selectivity coefficient for the j-th ion, j-th interfering ion for ai ion of primary ion of interest. So, the i here is the primary ion of interest, the j here is the interfering ion. So, selectivity coefficient is in the presents of j interfering ion. What would be the selectivity coefficient of j over i the primary ion of interest? That is how the selectivity coefficient is define. Times of aj which is activity of the j-th ion, which is the interpreting ion divided by n by z. $E = K + Slog\left(a_i + k_{i,j} a_j^{n/z}\right)$, n is the charge of ai or a primary ion of a interest and z is charge of you know the secondary ion or the interfering ion; j in this case. So, the derivation of the equation of course, is not within the scope of this course. But it does give a very good fairly good accurate estimate of the EMF, the modified EMF in the presents of j-th phase you know of ion which is interfering. So, if we have several such interfering specious and by the by this is again linear equation. Look at it put it in linear if you do not consider this is back it term here, or if you consider just to be just the differential concentration it is still a straight line with intercept and Nernst slope S. And when other irons interfere; that means, there are more than one irons which are interfering. In that case the equation will slightly change, still it will be in the Nernst equation form, it will modify to E equals K plus S log of ai plus K ij, aj to the power of N by z aj. Again let me reiterate here N is the charge or the valency of the primary ion i of interest here; z aj is the charge or the valance of the secondary ion or the interfering ion j in this case, plus K i K, a K times k to the power of n by z a k plus K il, al to the power of n by z al so on and so forth. All the phases are covered. $E = K + S\log\left(a_i + k_{ij} a_j^{\frac{n}{z aj}} + k_{ik} a_k^{\frac{n}{z ak}} + k_{il} a_i^{n/z\,al}\right)$ So, this is essentially an extension of multiple terms of the same series here that we showed before for expressing the modified EMF in the presence of interfering ion. So, K ij, K ik, K *il* etcetera are the selectivity coefficients of the j-th, k-th, i-th phase coefficients of for the j-th k-th i-th ions respectively.

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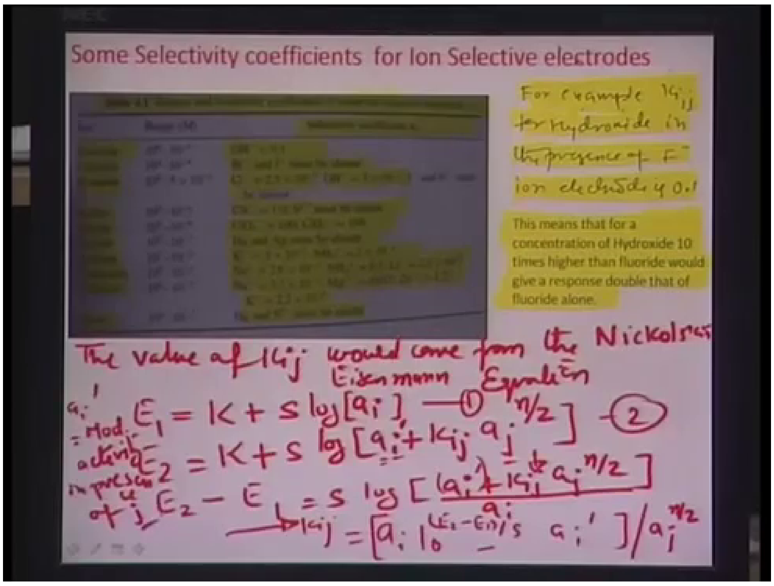

Some Selectivity coefficients for Ion Selective electrodes

For example K_{ij} for hydroxide in the presence of F^- ion electrode is 0.1

This means that for a concentration of Hydroxide 10 times higher than fluoride would give a response double that of fluoride alone.

The value of K_{ij} would come from the Nickolsky Eisenmann Equation

a_i' = Mod. activity in presence of j

$E_1 = K + S\log[a_i]$ — ①

$E_2 = K + S\log[a_i' + K_{ij} a_j^{n/2}]$ — ②

$E_2 - E_1 = S\log\left[\frac{(a_i' + K_{ij} a_j^{n/2})}{a_i}\right]$

$\longrightarrow K_{ij} = \left[a_i 10^{(E_2 - E_1)/S} - a_i'\right] / a_j^{n/2}$

$$E_1 = K + S\log\left(a_i\right)$$

$$E_2 = K + S\log\left(a_i + k_{i,j}a_j^{n/z}\right)$$

$$E_2 - E_1 = S\log\left[\frac{a_i + k_{i,j}a_j^{n/z}}{a_i}\right]$$

Essentially, if you look at some of the typical examples of a K ij values. It can be very apparently it is really mentioned in the stable 4.1 here; which talks about the ranges and selectivity coefficients of some ion selective electrodes. So, essentially if you want to measure of fluoride ion. So, we were talking about this a different selectivity coefficients in let me actually take you back into the slide again. So, the ranges and selectivity coefficients of some selective electrodes, ion selective electrodes I am mentioned in this table here 4.1. How to interpret this stable really, this here this given the K ij value. So, if you want to measure hydroxide which is the primary ion in this case, in the presents of fluoride the ion selectivity of hydroxide is only 0.1. If you want to measure bromine and iodine, chlorides really must be absent from the solution. So, that you could measure Bromium however, if you want to measure Chlorine there is a selectivity coefficient specially bromides are at represent. Similarly hydroxides you know the presents of bromides will offer K ij value, which is recognize in this table so and so forth.

So therefore, this table really is summary of what would be the selectivity of a primary ion of interest over the several interfering irons which are measured, which are mentioned here in this extreme left column of this particular table. And the selectivity coefficient are independently mentioned here, individually mentioned here in the third column of this particular table.

Let us also look at what the interpretation of this would be. So, if the K ij for the hydroxide the presents of the fluorides is just 0.1, it would mean that for a concentration of hydroxide 10 times higher than the fluoride, it would give a response double that of the fluoride alone. So, if the hydroxide is about 10 times more than the fluoride, then there would be corresponds which is double that of the fluoride alone. So, which is of significance, which is of some measurable significance. So therefore, you are measure in also means that if you measuring fluoride then if you are hydroxide, you need not bother till and until hydroxide is about 10 times more in concentration in the fluoride is. Let us also look at one more aspect how to determine the value of K ij and I would like to do some derivatives here. So, when we are talking about in the Nikolsky ions and equations, you know the value of K ij would come from the Nikolsky equation.

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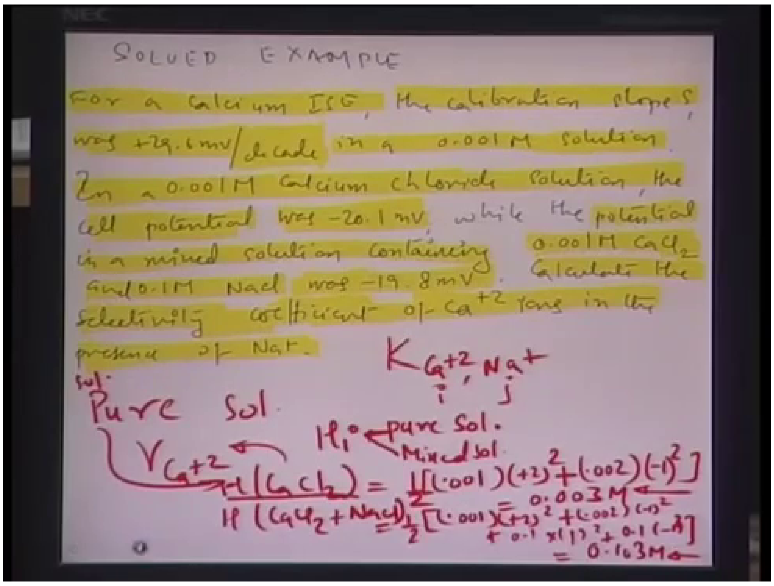

SOLVED EXAMPLE

For a Calcium ISE, the calibration slope S, was +29.1 mV/decade in a 0.001 M solution. In a 0.001 M Calcium Chloride Solution, the cell potential was -20.1 mV, while the potential in a mixed solution containing 0.001 M $CaCl_2$ and 0.1 M NaCl was -19.8 mV. Calculate the selectivity coefficient of Ca^{+2} ions in the presence of Na^+.

$K_{\underset{i}{Ca^{+2}}, \underset{j}{Na^+}}$

Sol.

Pure Sol.

$\gamma_{Ca^{+2}} \leftarrow \mu_i$: pure Sol. / Mixed Sol.

$\mu(CaCl_2) = \frac{1}{2}[(.001)(+2)^2 + (.002)(-1)^2] = 0.003M$

$\mu(CaCl_2 + NaCl) = \frac{1}{2}[(.001)(+2)^2 + (.002)(-1)^2 + 0.1 \times (1)^2 + 0.1(-1)^2] = 0.103M$

So let us suppose we have certain ion of interest i for which the EMF has been measure using Nernst equation as E1 is equal to K plus Nernst’s slope S times of log activity of the primary ion ai. When we add a secondary ion let say j with the selectivity coefficient K ij, E 2 here and the represented as K plus S log of ai plus K ij, a to the power of or aj to the power of n by z suppose. n and z of course the valance is ion i and ion j respectively. So, if you just try to calculate K ij here, it come out from subtracting equations 2 from 1 and we can get E2 minus E1 is S log of ai plus K ij, aj to the power n by z by ai right. And here this, this is actually the modified activity; let as assumed that this modified activity is ai dash. This is no longer ai, because a i is the activity of the ion in presence of a none other and a i dash is the modified activity of the ion in the presence of the phase j. So, if you solve this equation and trying to find out what K ij is from this equation, K ij can be return down as a i times of 10 to the power of E2 minus E1 divided by S minus a i dash divided by aj to the power of n by z; that is what K ij would be in this case. ai dash again I retreat is actually the modified or corrected activity of the mixed solution. So, let me write down somewhere that in this particular case, a ij, ai dash is modified activity in presents of i and j.

Since now we have more or less covered how to calculate the activity of a particular ion of interest in a solution and also we have seen methodological calculating selectivity coefficient. Now let us do a practical example where in we have let us a two participating solutions, and we have a data of the EMF form the pure solution as well as the mix phase. We are both the solutions are participating, both the ions are participating. And we try to calculate what the K ij of the selectivity coefficient would be.

So, let us look at the solved example here. Let suppose that you know the for a calcium ISC, for a calcium ion selective electrode. The calibration slope S is essentially plus 29.6 millivolts per decade. This word decades essentially means one order of concentration. So, the concentration is change by one order the log to be based enough it changed by one unit, and so therefore S essentially is nothing but plus 29.6 millivolts. It also makes sense because this is equal to if you look at this 59 millivolts divided by number of electrons transfer. N in this cases 2 because calcium can get oxidize 2 calcium plus 2 state and therefore, in that case also slope is plus 29.6 millivolts. So, this is essentially the calibration slope is in a point is 01 molar solution and. So, in a point 001 molar calcium chloride solution the self potential of a while you know measuring through the unselective electrode was measure to be 20.1 millivolts. Now we mix this calcium chloride solution with NaCl of salt solution in the following ratio.

So, and then measure the potential again. So the potential in the mixed solution containing 0.001 molar of CaCl2 and 0.1 molar of NaCl, was 19. 8 millivolts. So, the pure solution of the calcium chloride with ion selective electrode and calcium measures 0.001 molar. And the 1 with mix solution containing 0.001 molar of calcium chloride and point 1 molar of NaCl was minus 19.8 millivolts. So, we had to calculate the selectivity coefficient of Ca plus 2 ion in the presents of Na plus. So, the selectivity of the calcium plus 2 ions in the presents of Na plus has to be calculated. In other words if you look at the ion selective coefficient you are essentially calculating K Ca plus 2 Na plus this is the j-th ion, the interfering ion. This is the i-th ion. So, how do we calculated? So, to begin with the we have to first calculate in the activities of the calcium and sodium ions, in you know the pure solution and the mixed solution. So, let us first do the pure solution case.

So, in the pure solution, we have to calculate what gamma Ca plus 2 would be? And so for doing that we need ionic strength a mean ionic strength of pure solution and also mixed solution. So, ionic strength of CaCl2 half Ci Zi squared, Ci here is 0.001 if it is a pure solution times of plus 2 square the charge on the calcium of the valance calcium is plus 2 plus CaCl2. So, there are two chlorine atoms per molecule of CaCl2. So, the chlorine concentration would be exactly double 0.002 molar times of minus 1 square. This comes out to be equal to 0.003 molar. So, this is the ionic strength of the pure solution, which is needed to calculate the gamma Ca plus 2 pure. Let us also calculate the ionic strength of the mix solution, which as CaCl2 at NaCl both phases.

So, we have half times of the concentration of a CaCl2 is 0.001 molar as important in the mixed solution; plus 2 square plus 0.002 for the chlorine times of minus 1 square plus again 0.1 times of 1 square, 1 being the valance of the Nacl plus 0.1 times of minus 1 square. And this comes out to be effectively equal to 0.103 molar. So, 1 you know the mu for CaCl2 comes out to be 0.003 molar; and for mixed solution the mean ionic strength comes out to be 0.103 molar. After doing this let us find out that in the pure solution, what is the activity coefficient of the Ca plus 2.

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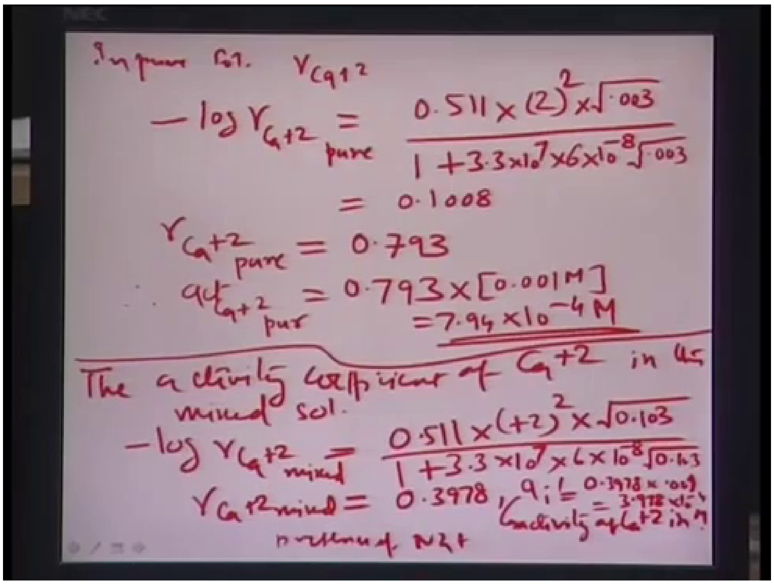

In pure sol. $\gamma_{Ca^{+2}}$

$$-\log \gamma_{Ca^{+2}\,pure} = \frac{0.511\times(2)^2\times\sqrt{.003}}{1+3.3\times10^7\times6\times10^{-8}\sqrt{.003}}$$

$$= 0.1008$$

$$\gamma_{Ca^{+2}\,pure} = 0.793$$

$$\therefore act_{Ca^{+2}\,pur} = 0.793\times[0.001M] = 7.94\times10^{-4}M$$

The activity coefficient of Ca^{+2} in the mixed sol.

$$-\log \gamma_{Ca^{+2}\,mixed} = \frac{0.511\times(+2)^2\times\sqrt{0.103}}{1+3.3\times10^7\times6\times10^{-8}\sqrt{0.103}}$$

$\gamma_{Ca^{+2}\,mixed} = 0.3978$, $a_i = 0.3978\times.001 = 3.978\times10^{-4}$ (activity of Ca^{+2} in M)

[illegible] of Na^+

So, in pure solution the activity coefficient of Ca plus 2 can also be represented by the following: minus log of gamma Ca plus 2 pure let us indicate this is pure, equals 0.511 which is the parameter a, which we calculated before. Plus zi square in this case it is plus 2 squared valance and calcium is plus 2 times of root over the mean ionic strength which was found out in the earlier equation to be 0.003 molar divided by 1 plus 3.3, 10 to the power 7; which is also the value of the B parameter in the particular equation into we have to really locate what is the ion size parameter in this case. And if you just go back and look into what that parameter is? The ion size parameter for calcium plus 2 ion as you can see here in this case is closed 600 picometers; so this is above 600 picometers. So 6, 10 to the power minus 8 centimeters.

Again I would like to retreat that all these system of equations is based on CGS units. So, we need to take in the value in centimeter. So, 6, 10 to the power of minus 8 is the ion size parameter a in this case types times root of 0.003, the mean ironic strength. So, this comes out to be equal to 0.1008. So, essentially taking entire logs on both sides the gamma value you know the selectivity coefficient of the pure Ca plus 2 comes out to be equal to 0.793 as in this particular case. $-\log \gamma_{Ca^{+2}} pure = \frac{0.511 \times (2)^2 \times \sqrt{0.003}}{1+3.3 \times 10^7 \times 6 \times 10^{-8} \times \sqrt{0.003}} = 0.1008$ So, in pure solution therefore, if we see what is the ionic activity of the calcium plus 2 ions. So, the ai value for the Eisenman equation, it comes out to be equal to act Ca plus 2 pure the gamma Ca plus 2 pure times of the concentration; concentration in this cases 0.001 molar. So, it comes out to be 7.94, 10 to the power of minus 4 molar. That is what in the activity of the pure calcium ions is in pure solution. $\gamma_{Ca^{+2}} pure = 0.793$

$$act_{Ca^{+2}} pure = 0.793 \times 0.001 M = 7.94 \times 10^{-4}$$

Let us simultaneously find out what is the ai dash; that means, the activity of the calcium plus 2 ions in the presents of Na plus. So, in order to do that in the 2nd phase of this question we need to actually see what is the activity coefficient for Ca in the mixed solution. So, we find out the activity coefficient of Ca plus 2 in the mixed solution. So, we have in the mix solution minus log of gamma Ca plus 2 and let us call this phase mixed phase equals 0. 511 which is the a parameter time of plus 2 square again. Because z is plus 2 essentially into or a product multiplied by the mean ionic strength in the mixed phase which is 0.103 as calculated before if we remember, divided by 1 plus 3 point 3, 10 to the power of 7 which is a in the B parameter times of again. In the calcium ion of course, as the ion size parameter of 600 picometer. If we just decide for come in back last slide 6 into 10 to the power of minus 8 times of the root of 1.03, 103; root of 0.103. So, the gamma Ca plus 2 in the mixed phase in this manner comes out to be equal to 0.3978 and if you look at the a i dash value; that means, the activity of C a plus 2 in presents of N a plus. That comes out to be equal to essentially 0.3978 times point 001, which is a also the morality of the CaCl2 in the mixed solution and that is 3 point 987 into 10 to the power of minus 4 molar. That is what the mixed activity or activity of C a plus 2 a phases in the mixed solution.

$$-\log \gamma_{Ca^{+2}} mixed = \frac{0.511 \times (2)^2 \times \sqrt{0.103}}{1+3.3 \times 10^7 \times 6 \times 10^{-8} \times \sqrt{0.103}}$$

$$\gamma_{Ca^{+2}} mixed = 0.3978$$

$$act_{Ca^{+2}} mixed = 3.978 \times 10^{-4}$$

So, going to the second part of the problem, let us find out what is the aj value. That is the changes case being the sodium plus ion or Na plus ion the aj value essentially is activity of the N a plus the presents of Ca plus 2. So we calculate that that here.

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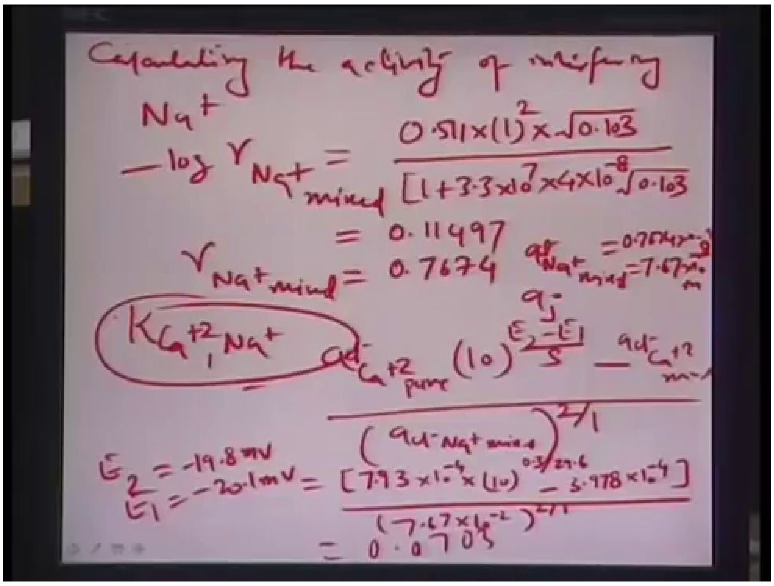

Calculating the activity of interfering Na^+

$$-\log \gamma_{Na^+_{mixed}} = \frac{0.511\times(1)^2\times\sqrt{0.103}}{[1+3.3\times10^{7}\times4\times10^{-8}\sqrt{0.103}}$$

$= 0.11497$

$\gamma_{Na^+_{mixed}} = 0.7674$ $\quad a_{Na^+_{mixed}} = 0.7674\times \quad = 7.67\times$

$$K_{Ca^{+2},Na^+} \quad \frac{a_{Ca^{+2}_{pure}}(10)^{\frac{E_2-E_1}{S}} - a_{Ca^{+2}_{mixed}}}{(a_{Na^+_{mixed}})^{2/1}}$$

$E_2 = -19.8$ mV

$E_1 = -20.1$ mV $= \dfrac{[7.93\times10^{-4}\times(10)^{0.3/29.6} - 5.978\times10^{-4}]}{(7.67\times10^{-2})^{2/1}}$

$= 0.0705$

So, calculating in the next phase the activity of the interfering ion. Here the ai dash is ai aj are all according to the Eisenman Nicholi, Nicolsky-Eisenman equation. Which we are discuss just about 2-3 slides back. So, essentially the interfering ion here is N a plus. So, for the Na plus we have minus long gamma Na plus in the we call it mixed again because the Na plus is present on the mix solution is equal to 0.511; a parameter times of z square, z in this case is plus 1 because Na is a univalent ion. So, Na plus is a univalent. So, plus 1 square times of root of mu which is again it is does not get altered, mean ionic strength again same in the mixed solution 0.103 whole under the root. And this is actually divided by 1 plus 3.3, 10 to the power of minus; 10 to the power 7, which is B parameter the times of the value of Na the ions size parameter of Na which is about 400 picometers from the table as we have done before.

So this is 4, 10 to the power minus 8 centimeter again the CGS units are to be used. Root over 0.103 and this comes out to be equal to 0.11497. So therefore, the gamma N a plus in the next phase of the activity coefficient of the sodium ion in the mixed phase comes out to be 0.7674; or the activity of the sodium ion a c t N a plus in the mixed phase comes out to be the equal to 0.7674 into 0.1, which is 7.67, 10 to the power minus 2 molar. That is what the activity of gamma of Na plus in the mixed phase S.

$$+¿\,mixed=\frac{0.511\times(1)^2\times\sqrt{0.103}}{1+3.3\times10^{7}\times4\times10^{-8}\times\sqrt{0.103}}=0.11497$$

$$Na^{¿}-\log\gamma_{\square}$$

$$+\text{¿}\, mixed=0.7674$$
$$Na^{\text{¿}}\gamma_{\square}$$

$$+\text{¿}\, mixed=0.07674$$
$$Na^{\text{¿}}\, act_{\square}$$

So, this is corresponding to also aj. So, we have pretty much everything which we need for the Nicolsky-Eisnman equation solution and we need to find out what the ion selectivity coefficient of K Ca plus 2 is over N a plus in the mixed phase. And that come out by the equation ai which is a Ca plus 2 pure, if you remember correctly the activity of Ca plus 2 pure times of 10 to the power of E2 minus E1 by S. If you remember from the question earlier the E2 was given as minus 19.8 millivolts, that is the potential generated by measurement along the mixed phase of the next solution. And E1 in the potential in the pure solution was given as minus 20.1 millivolts; E2 minus E1 by S really is a nothing but point 3 divided by point 29 point 6.

So, therefore, this 10 to the power E2 minus E1 by S minus ai dash which is the modified activity of Ca plus 2; that means, this is the mixed phase activity divided by a j which is to the power n by z. And aj here is the activity of the Na plus mixed phase to the power of n by z; n is plus 2 mind you because this is valance of c a primary ion of interest and z is the valance of secondary ion of the interfering ion is 1 as in case of Na plus.

So, if you put back all the values here comes out to be equal to 7.93; 7 point 93, 10 to the power of minus 4 times 10 to the power of and you calculate this as 0.3, 0.3 divided by 29.6 millivolts minus 3.978, 10 to the power of minus 4. Which are just these values have been all calculated earlier, if you may recall; divided by this 7.67, 10 to the power of minus 2 times of or to the power of 2 by 1 that is 2. So, this comes out to be equal to 0.0703. So, that is what the K Ca plus 2 in the presents of the interfering ion Na plus is going to be. What really it means? Is that the solution containing all most 14 times as much Na plus as Ca plus 2 give a response to which is double that of the value for Ca plus 2 ions alone. So, defiantly Na plus ion is a weekly interfering ion to Ca plus 2.

$$+\text{¿}=\frac{act_{Ca^{+2}}\, pure\,(10)^{(E2-E1)/S}-act_{Ca^{+2}}\, mixed}{\left(act_{Na^{+2}}\, mixed\right)^{2/1}}=0.0703$$
$$+,Na^{\text{¿}}Ca^{\square}$$
$$K_{\square}$$

So, in conclusion what i would like to certain here is, that in these kind of problems you get a very good idea or a very good feel of what would be the level of interference of a certain ion over primary interest. This is defiantly very helpful for designing ion selective electrodes. So, you know at the towards the end of a, we are almost towards the end of this lecture and I would like to discuss again what will take up in the next lecture. So, we have now by enlarge seen detailed derivations about you know ionic activity, understood and realize the importance of how it is helpful and designing ion selective electrodes, and also how we can predict the EMF of a solution which has all these mixed phases ions of different kind some interfering some primary ions of interest.

Now, coming to some physical, some physically realizable electrodes etcetera, the natural question is that can be really look at some of the senses more closely and how the mechanisms help them to sense, things like gases you know, or things like certain metabolized chemicals. The senses that often are used medical dynastic area where the problems related to increase in urea with in the blood, or you know increase in blood glucose etcetera. Quickly recorded and sent almost real time investigation is some time done on the bed side, as we have been talking out the earlier lecture before. So, in the next lecturer, I would like to cover more or less some details about what is that interface of a these, some of the senses with different metabolized of a interest related to human body, human blood or some other gases which may be effective for designing a gas cancel may be eventually. And then we would like to look at how we can further naturalize then to have an electro chemical response and understand how you know in MEMS way, in a micro engineering manner or using micro engineering tools you could develop something sensitive at to detect a pick up analyze of interest. So, would like to close this lecture with this.

Thank you.