Bio - Microelectromechanical Systems

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Module No. # 01

Lecture No. # 09-10

Biomicroelectromechanical Systems

Welcome back to this 10th lecture of BioMEMS. Just to review what we were talking in the last lecture, we try to generate an equation were in the free energy per mole of the system which is also expressed as KT ln gamma i; gamma i being the arithmetic coefficient was equated to the total amount of work that was needed to bring a charge ZiE into minus ZiE into central ion of interest which is a plus ZiE charge. In other words, in order to give a charge its counter ionic cloud the amount of work done is given by this integral of d w. So, from the equation, we try to get an expression in terms of gamma i as the following.

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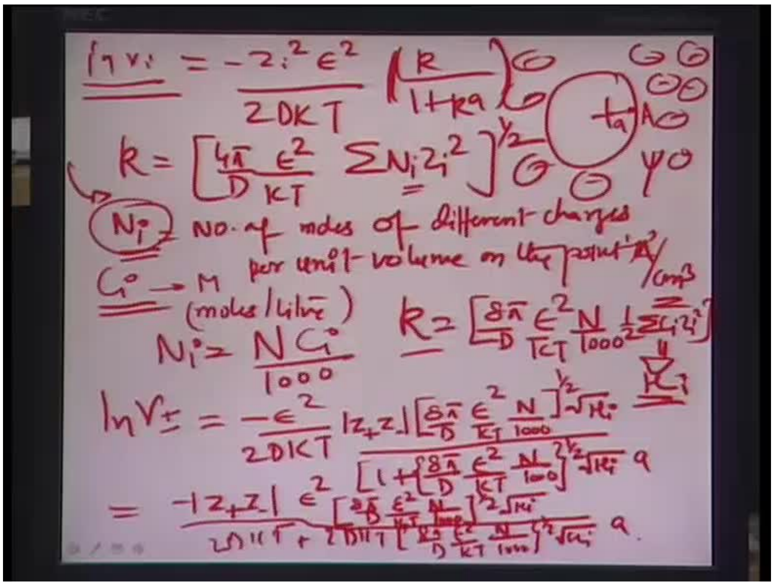

$$\ln \gamma_i = \frac{-z_i^2 \epsilon^2}{2DKT}\left(\frac{k}{1+ka}\right)$$

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

N_i = No. of moles of different charges per unit volume on the point 'A'/cm³

$C_i \to M$ (moles/litre)

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

$$k = \left[\frac{8\pi}{D}\frac{\epsilon^2}{KT}\frac{N}{1000}\frac{1}{2}\sum C_i z_i^2\right] \Downarrow \mu_i$$

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

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

So, l n gamma i, natural log of gamma i - the activity coefficient - also came equivalent to minus Zi square epsilon square by twice DKT into the counter ionic radius k by 1 plus small k times of a - a here was the ion size parameter; it is an indication of the tentatively what is the size of the central ion of interest.

Also we know that k essentially is nothing but, 4 pi by D, E square by kT sigma Ni Zi square to the power of half. In other words, we can express this in a more appropriate manner by assuming that what is really Ni?

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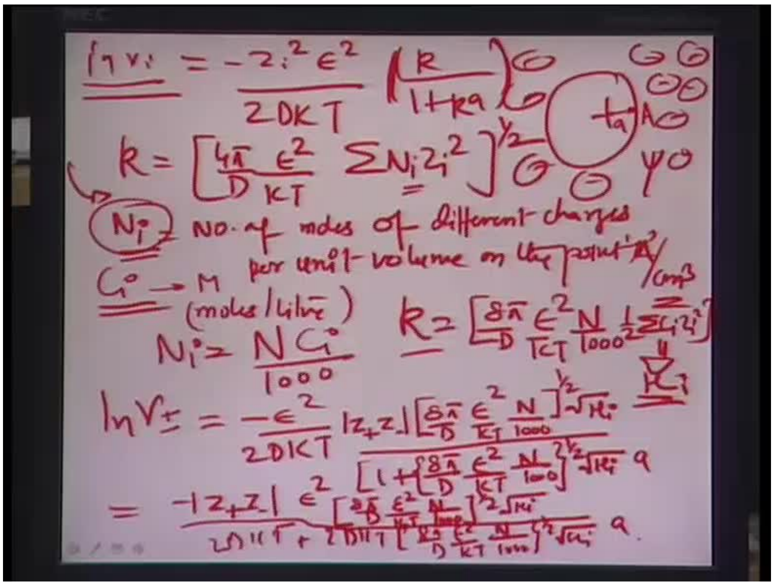

$$\ln \gamma_i = \frac{-z_i^2 \epsilon^2}{2DkT}\left(\frac{\kappa}{1+\kappa a}\right)$$

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

N_i = No. of moles of different charges per unit volume on the point 'A' /cm³

$C_i \rightarrow M$ (moles/litre)

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

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

μ_i

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

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

Ni is essentially the number of moles of different charges whether it is positive or negative its different charges - you remember the way we talked about the subscript i in our lectures before - per unit volume on the point A. We were talking about a central ion and a point A, which was close by where the potential is phi and then a negative ion atmosphere, which was all the way around it just for recapitulating what we had done earlier. So this was the point A, essentially this here was the point A when which was at a distance of small a, from the center of this charge; this was the point A (Refer Slide Time: 03:26), the radius here is small a.

We can really express this in terms of the concentration of the various ions that are there in the solution and from which we formulate it, the mean concentration. What we try to estimate this as since Ci is also in terms of mole - molar or moles per liter - and this Ni was per centimeter cube because it was all CGS units which were used at the beginning of the 19th century to explain at least problems - majority of the problems - in this chemistry or related to charge essentially in chemistry.

Here, we could consider the number of moles per unit volume Ni to be a product of the Avogadro number N, which is 6.023 into 10 to the power 23 the numbers in mole divide into the concentration Ci by 1000cc or 1000 centimeter cube makes 1 litre. From these two, from this kind of an expression the k could be written as really 8pi by D epsilon square by kT N by 1000 half Ci Zi square and this Ci is nothing but, the mean ion concentration of i. So, we can call it mu i.

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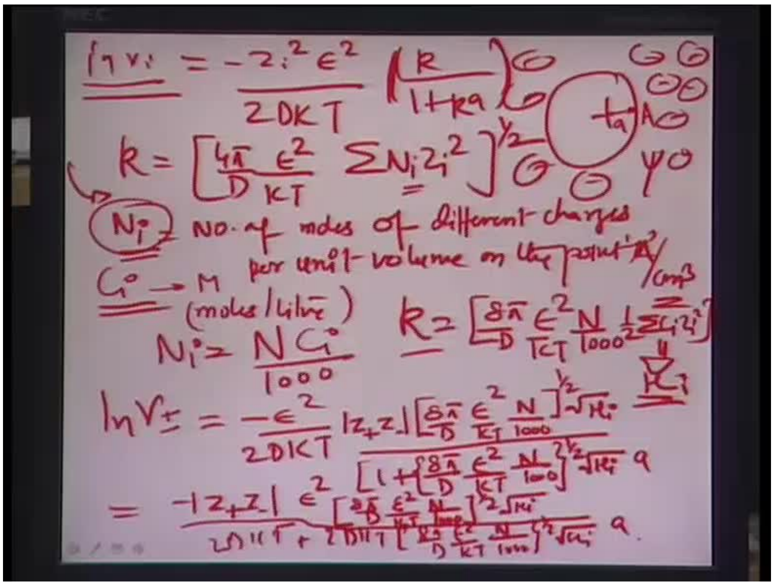

$$\ln \gamma_i = \frac{-z_i^2 \epsilon^2}{2DKT}\left(\frac{k}{1+ka}\right)$$

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

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$C_i \rightarrow M$ (moles/litre)

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$$k = \left[\frac{8\pi}{D}\frac{\epsilon^2}{KT}\frac{N}{1000}\frac{1}{2}\sum C_i z_i^2\right] \Downarrow \mu_i$$

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

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

Today, we try to go ahead in this and try to find out what this ln gamma i would be in terms of this final and full expression for k and we get that ln gamma i. Now, I would like to change the subscript i by its essence the way that we had started all these things we had assumed i could be either positive or it could be negative.

So, I write gamma plus minus here is equal to minus epsilon square by 2 DKT times of Z plus Z minus and modulus of that, so for the principle of electro neutrality the positive and negative charges and otherwise electrically neutral medium would be equal exactly opposite. 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, you have to take the magnitude of Z plus Z minus times of k by 1 plus k into a and k here comes out to be equal to 8 pi, let me just go ahead and shift this down a little bit so that it will be convenient.

So this is Z plus Z minus mod times of k, which is 8 pi by D, 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 should be second bracket, whole half times of root mu i times of a where a is the ion size parameter. This gives us very interesting way of representation, we could couple this all together and just write it as in the following manner; Z plus Z minus of course, modulus and epsilon square is taken here, I think the value of 8 pi by D epsilon square by KT, N by 1000 half root mu i and in the denominator you have twice DKT plus twice DKT times of 8 pi by D E square by KT, N by 1000 whole half root of mu i times of a.

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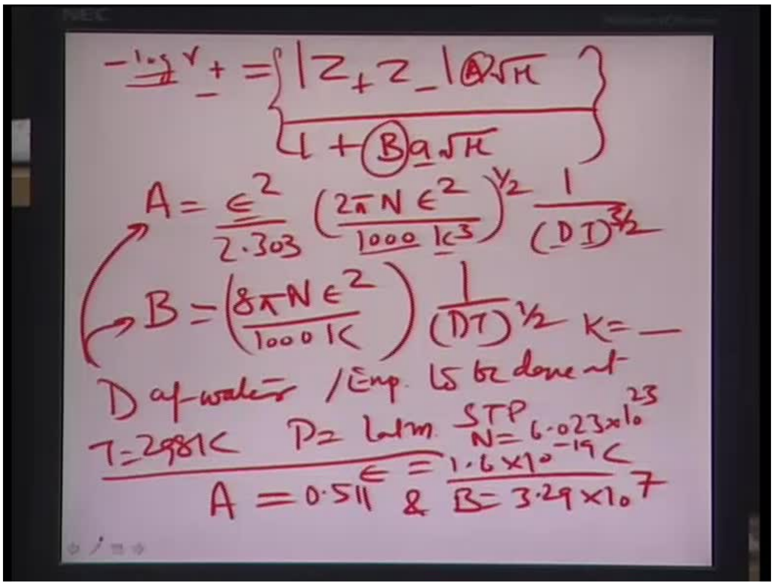

$$-\log \gamma_{\pm} = \left\{ \frac{|Z_+ Z_-| \boxed{A} \sqrt{\mu}}{1 + \boxed{B} a \sqrt{\mu}} \right\}$$

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

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

D of water / Exp. is to be done at STP

$T = 298K$ $P = 1$ atm $N = 6.023 \times 10^{23}$

$\epsilon = 1.6 \times 10^{-19} C$

$A = 0.511$ & $B = 3.29 \times 10^{7}$

Therefore, we can write this expression in a little different manner, so that it can be more simplified. You have minus log of gamma plus minus and you can write this as Z plus Z minus a times of root mu divided by 1 plus B times of, therefore, this can be represented as 1 plus B times of, a times of root of mu. These a s and B s are just it is like for overall convenience we can report this and if you really represent the whole thing in terms of a mind there is a log here which is equal to 2.303 ln, so 2.1 by 2.303 ln value.

Essentially A here is nothing but, square of E by 2.303 and I am just simplifying and writing it down, which is convenient 2 pi N epsilon square by 1000 k 3 this is just by simplification that you can represent this particular form with 1 plus b times a root mu and here Zi square times of a times of root of mu, Zi square is again modulus of Z plus into Z minus times. So, this raise to the power of half times of 1 by DT to the power of 3 by 2, that is how the A can be represented and 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 for water, in most of the cases, the solutions which are being investigated is essentially an aqueous based solution of these ions. The basic medium there is water; 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. So, 298 Kelvin 1 atmosphere pressure this kind of condition and then of course, N value is a universally acclaimed fixed value 6.023 10 to the power of 23 numbers of atoms or molecules or charges as in this case.

Therefore, we can calculate the values of A and B, if you look at and also the E here is 1.6 10 to the power of minus19 coulomb, charge of 1 electron. So, the A it kind of encompasses all these constant values you have a k value for the Boltzmann constant, you put the Boltzmann constant value 1000 N, you have E square and you have dielectric constant for water and temperature 298 Kelvin.

You can compute all these values and it comes out to be 0.511 and B comes out to be 3.29 into 10 to the power of 7 relatively a very large value. But the very fact is that because, this B is also in product with ion size parameter which maybe a few nanometers and we will be investigating and estimating a few tables later on for the ion size parameter A. Therefore, the equation and the gamma value would hold consistency.

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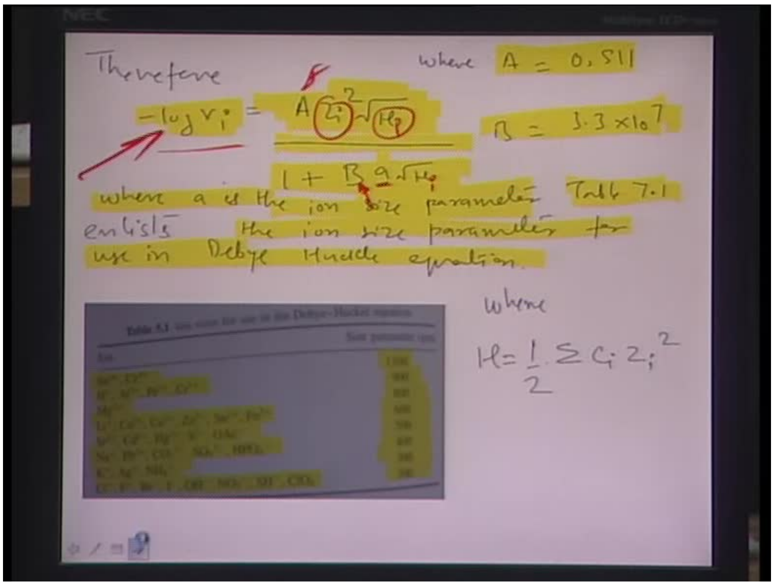

Therefore

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

where $A = 0,511$

$B = 3.3 \times 10^7$

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

where

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

Therefore, the whole equation can really be written down in the terms of minus log gamma i, as you are seeing here; equals A times of Zi square Zi is being the positive or the negative charge divided by 1 plus B a root of mu, where A is calculated to be 0.511, B is calculated to be 3.3 into 10 to the power 7 by assuming STP - Standard Temperature Pressure and the various parametric values for N Avogadro number, epsilon, electronic charge so on so forth.

So, a is very interesting proposition here, a as you see in this particular area here, 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, selenium ions or tin ions of quadravalent state has an ion size parameter of about approximately 1100 pico meters. Similarly, you have H plus, Al plus 3, Fe 3 plus and Cr minus these values they have about 900 pico meters. Essentially, these all ion size parameters have been investigated revaluated from the Debye Huckle theory and they are tabulated and they are used often on for all sorts of experiments.

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

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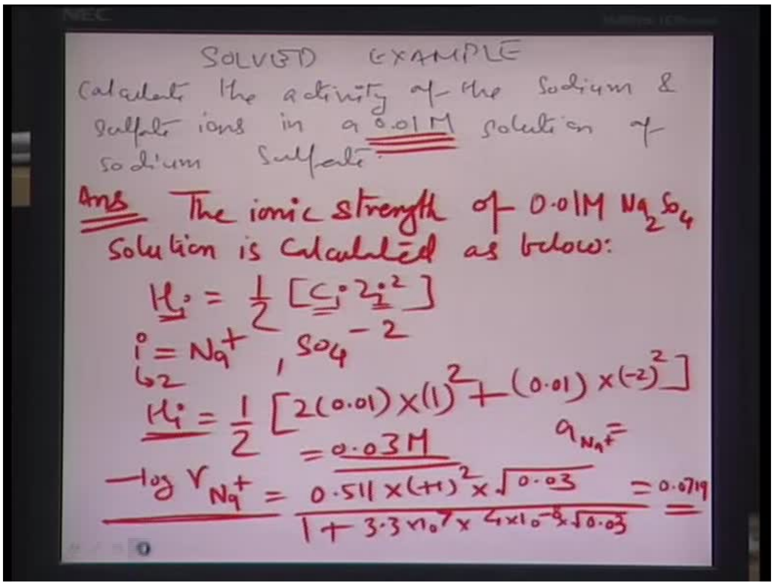

SOLVED EXAMPLE

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:

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

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

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

$= 0.03M$

$a_{Na^+} =$

$$-\log \gamma_{Na^+} = \frac{0.511 \times (+1)^2 \times \sqrt{0.03}}{1 + 3.3 \times 10^7 \times 4 \times 10^{-8} \times \sqrt{0.03}} = 0.0719$$

Having said that, let us actually look into a little bit of a kind of solved example were we talk about how to calculate the activity of sodium and sulfate ions independently. Let us say, 0.01 molar solution of sodium sulfate. You have a case, were 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 the Debye Huckle set of equations.

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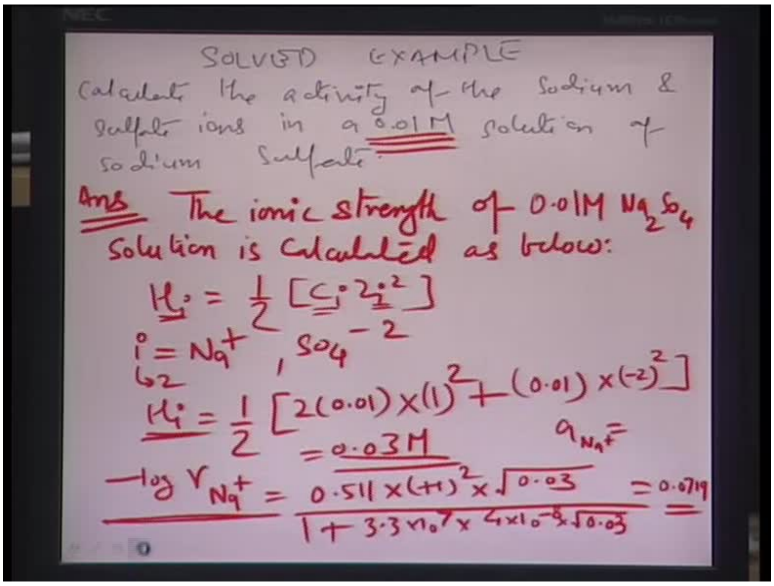

SOLVED EXAMPLE

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

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

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

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

i=2

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

$$= 0.03M \qquad a_{Na^+} =$$

$$-\log \gamma_{Na^+} = \frac{0.511\times(+1)^2\times\sqrt{0.03}}{1+3.3\times10^7\times 4\times10^{-8}\times\sqrt{0.03}} = 0.0719 =$$

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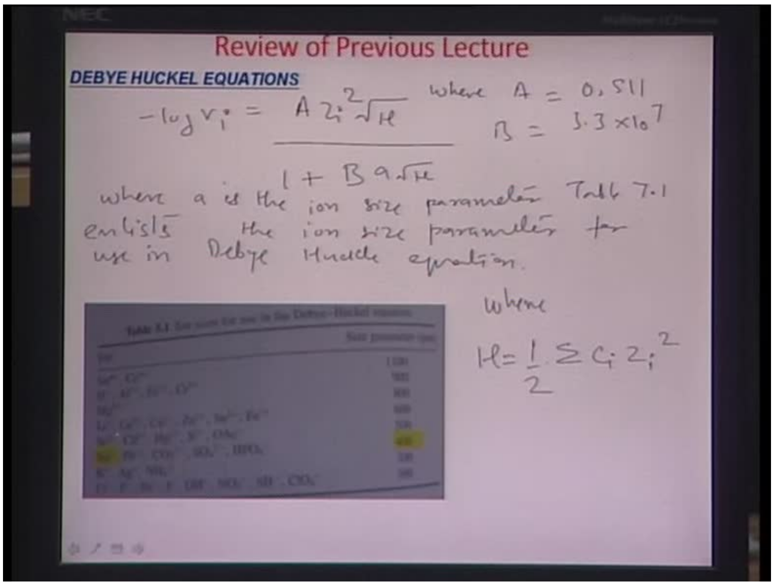

Review of Previous Lecture

DEBYE HUCKEL EQUATIONS

$$-\log \gamma_i = \frac{A z_i^2\sqrt{\mu}}{1+Ba\sqrt{\mu}}$$ where $A = 0.511$, $B = 3.3\times10^7$

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

where

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

Let us try to solve this, we have a case where we need to find out the activity given the ionic strength or given the molarity of the sodium sulfate solution. The ionic strength of the sodium sulfate of the 0.01 molar Na 2 So 4 sodium sulfate solutions is calculated as below you have half Ci Zi square. How many i s are there, there is a Na plus and there is a So 4 minus 2 so there are 2 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 the sodium sulfate solution has a molarity mind you of 0.01.

There are 2 sodium ions every molecule of Na 2 So 4 and therefore, you have the overall molarity of Na plus as 0.02 molar. The concentration times of the square on the valancy which is plus 1 in case of sodium plus and this is essentially a summation term because it is accumulative of all the positive and negative charges. Now, you have the concentration for So 4 which is only 1 molar or which is only 1 in the molecule. So you have a concentration of 0.01 molar times of, now the charge here is minus 2 because So 4 or sulfate ion bivalent ion essentially square of that, so this comes out to be from calculations equal to 0.03 molar. So, this is the mean ionic strength of this sodium sulfate solution.

Once the mean ionic strength is calculated rest of the things are easy. You just need to calculate minus log of gamma Na plus in this case, which would be equal to the 0.511 the a term, terms of times of the square of the valancy on the sodium which is plus 1 square times of root over mu i; where mu i is 0.03 molar and divided 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 obtained from the table as given before here. The sodium Na plus essentially if you look at this particular zone here has an ion size parameter of about 400 pico meters or 4 into 10 to the power of minus 10 meters or 4 into 10 to the power of minus 8 centimeters.

Since we are actually using the CGS units for calculating everything here, we would take the ion size parameter A as 4 into 10 to the power of minus 8 centimeters times of the root of 0.03 molar. This comes out to be equal to 0.0719 that is what the ionic strength of the negative log of the ionic activity of Na plus is; so let us calculate and do the same kind of calculation for the So 4 ion.

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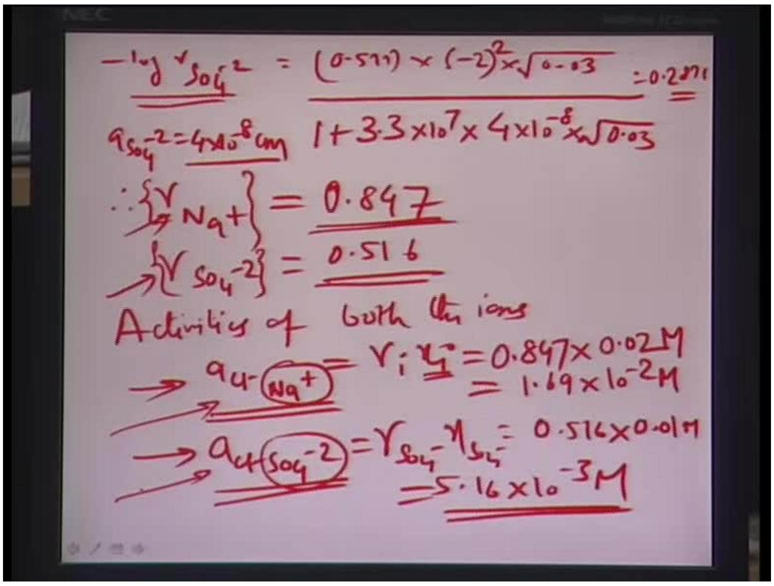

$$-\log \gamma_{SO_4^{2}} = \frac{(0.511)\times(-2)^2\times\sqrt{0.03}}{1+3.3\times10^{7}\times4\times10^{-8}\times\sqrt{0.03}} = 0.2871$$

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

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

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

Activities of both the ions

$a_{ct}(Na^+) = \gamma_i y_i = 0.847\times0.02M = 1.69\times10^{-2}M$

$a_{ct}(SO_4^{-2}) = \gamma_{SO_4^-} \eta_{SO_4^-} = 0.516\times0.01M = 5.16\times10^{-3}M$

In case of So 4, the activity can be, the equation can be written down as minus log gamma So 4 minus 2 equal to 0.511 that is the A parameter, A aspect, the coefficient A times of square on the valancy of sulfate and sulfates valancy 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 the power 7 times of the radius of So 4 ion which again through this particular figure. Here So 4 minus 2 and Na plus are more or less in the same size domain is about 400 pico meters.

Essentially, it means the ion size parameter a, for So 4 minus 2 should be about 4 10 to the power minus 8 centimeters 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 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 0.03 and essentially that is calculated to be 0.2876.

Taking antilog on the both equations solved earlier the activity of the sodium ion comes out to be 0.847 and the activity of the sulfate ion So 4 ion minus 2 in this case comes out to be 0.516. If we look at these are the activity coefficients; let me just reiterate the activity coefficient of the sodium ion comes out to be 0.847 and the activity coefficient of the So 4 ion comes out to be a 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 it with the ion size parameter.

Let us just get a different name here for convenience. Let us say, we have we just write acti instead of act Na plus equals gamma i times of xi as you know xi is the ionic concentration of the particular analyte. In case of sodium you have 0.847 as the gamma i and the xi as you know in this case because you have 2 atoms per molecule and the overall concentration is 0.01. For sodium the concentration is 0.02 molars.

The activity in this case is only about 1.69 10 to the power of minus 2 molar and in case of So 4 the activity So 4 minus 2 can be the gamma, So 4 minus 2 times of concentration of So 4 minus 2, which is 0.516 to above times of 0.01 molar. Mind you in 1 molecule there is only 1 So 4 atom which is present; therefore, its concentration is only same as that of the Na 2 So 4 solution. This comes out to be equal to 5.16 10 to the power of minus 3 molar. That is how you are able to calculate the activity of Na plus and So 4 minus in a sodium sulfate solution by looking at the various aspects.

Now, what you would be interested to look at here is that if you may just see that the activities of both are different. Therefore, Na plus is a more active ion than So 4 minus, so in such kind of situations if there is a presence of both ions that is Na plus and so 4 minus there is a tendency of the electrode to be heavily interfered by the Na plus ion if you are detecting sulfate ions.

You have to be careful in order to create a situation where the Na plus ion is blocked in a manner, so that its activity is also blocked and the ion selective electrode can only specifically pickup; So 4 minus ion in the presence of Na plus ion minus 2 ion in case of a So 4, minus 2 ion in place of or in the presence of Na plus ion.

You have a fairly good idea about activity coefficients at this time and how they would be calculated. Once, we are actually done with these activity coefficients what is very important to find out here is that, due to these activities what is really the change in the EMF the measured potential of such a solution, where you have about more than 1 species of ions with interfering ions as well as the primary ion of interest.

Essentially the E value, the potential value, would change because of these participating in other kind of interfering kind of ions. There is a set of equations called Nicolskii-Eisenmann equation which is used for predicting the EMF value of j such components together in a solution - in an electrochemical solution and the effects of those components on the measured EMF of such a solution.

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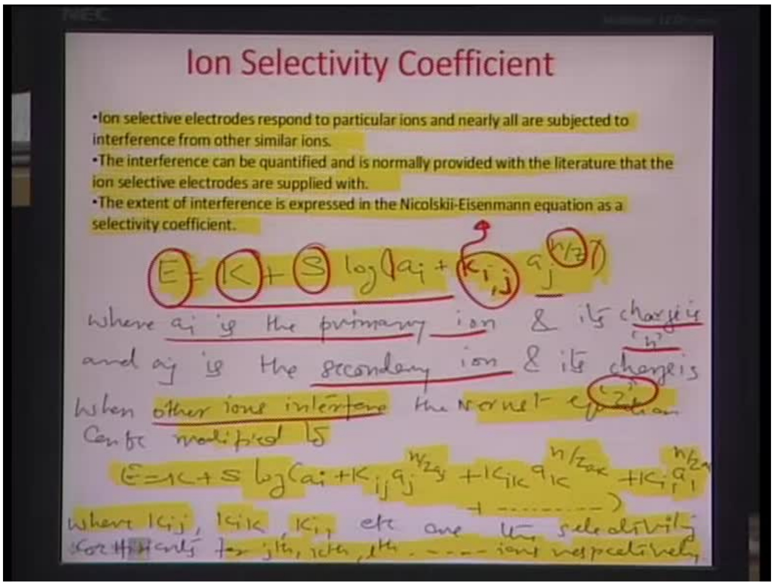

Ion Selectivity Coefficient

- 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.

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

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

For designing ion selective electrodes, the very important factor is the ion selectivity coefficient and so it is a kind of quantification of the interference. In a nutshell, we can summarize all this as that ion selective electrode responds to particular ions and nearly all are subjected to interference from other similar ions. The interference can be quantified is normally provided with a literature that ion selective electrodes are supplied with and the extent of interference is expressed by this set of equations Nicolskii-Eisenmann equation as a selectivity coefficient.

The EMF of given out by such a solution which has more than 1 ion of a participating ions with 1 ion of interest and the remaining interference ions can be also written as K plus S log of a i 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 will be demonstrating, I will be just showing a table which we will be talking about several such values of k ij, which means that the selectivity coefficient for a jth interfering ion for i primary ion of interest. So i here is the primary ion of interest and the j here is the interfering ion, so selectivity coefficient is in the presence 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 defined.

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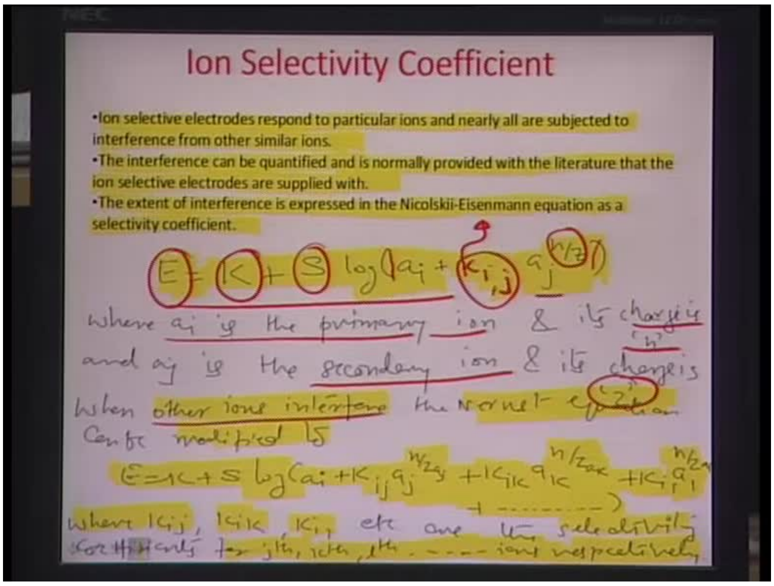

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- The extent of interference is expressed in the Nicolskii-Eisenmann equation as a selectivity coefficient.

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

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

Times of a j which is the activity of the jth ion, which is the interfering ion divided by n by z; n is the charge of a i or the primary ion of interest and z is the charge of the secondary ion or the interfering ion j in this case. The derivation of this equation of course, is a not within the scope of this course but, it does give a very good fairly good accurate estimate of the modified EMF in the presence of a jth phase of ion which is interfering. So if you have several such interfering species, by the by, this is again a linear equation if you look at it pretty in linear if you do not consider this bracketed term here or if you consider this to be just the differential concentration it is still a straight line with an intercept and Nernstian slope S. When other ions interfere that means there are more than 1 ions which are interfering in that case the equation will slightly change still it will be in the Nernst equation form but, it will be modified to E equals K plus S log of a i plus k ij a j to the power of n by z a j.

Again let me reiterate here, n is the charge or the valancy of the primary ion i of interest here, z a j is the charge or the valancy of the secondary ion or the interfering ion j in this case plus k ik a k times a k to the power of n by z a k plus k il a l due to the power of n by z a l so on so forth up till all the phases are covered. 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 an interfering ion.

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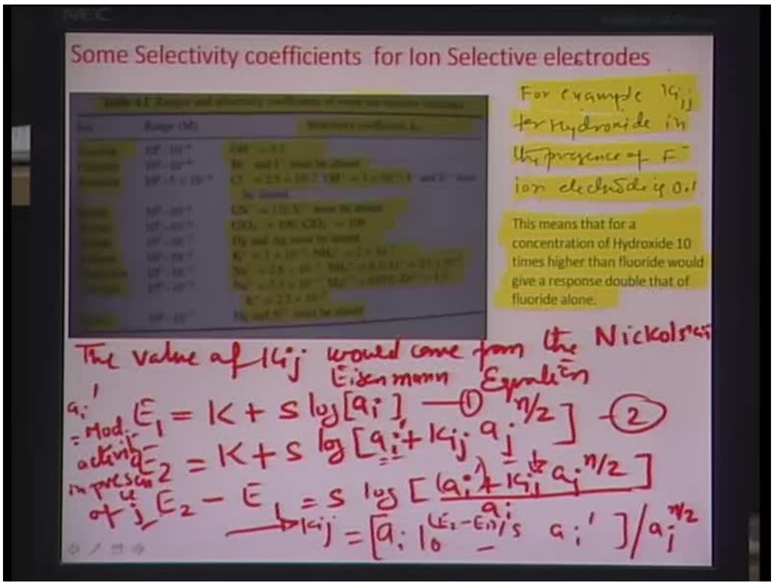

Some Selectivity coefficients for Ion Selective electrodes

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 Nickolski Eisenmann Equation

a_i' = Mod. activity in presence of j

$$E_1 = K + S \log[a_i'] \quad ①$$

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

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

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

So k ij, k ik, k il etcetera are the selectivity coefficients of the jth, kth, ith phase coefficients for the jth, kth, ith ions respectively. Essentially, if you look at some of the typical examples of k ij values it can be very apparently it is really mentioned in this table 4.1 here (Refer Slide Time: 30:30), which talks about the ranges and selectivity coefficients of some ion selective electrodes. Essentially if you want to measure a fluoride ion, we were talking about these different selectivity coefficients and let me actually take you back into the slide again.

The ranges and selectivity coefficients of some selective electrodes ion selective electrodes are mentioned in this table here 4.1. How to interpret this table really? This here is giving the k ij value, so if you want to measure hydroxide which is the primary ion in this case. In the presence 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 bromine and iodine.

However, if you want to measure chlorine there is a selectivity coefficient especially bromides are present. Similarly, hydroxides in the presence of bromides will offer a k ij value which is written in this table so on so forth. Therefore, this table really is a summary of what would be the selectivity of a primary ion of interest over the several interfering ions which are mentioned here in this extreme left column of this particular table. The selectivity coefficients are independently mentioned here or 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 hydroxide in the presence of fluorides is 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. If the hydroxide is about 10 times more than the fluoride then there would be a response which is double that of the fluorine alone, so which is of some measurable significance. Therefore, you are measuring it also means that if you are measuring fluoride and if you have hydroxide you need not bother till and until the hydroxide is about 10 times more in concentration than the fluoride is.

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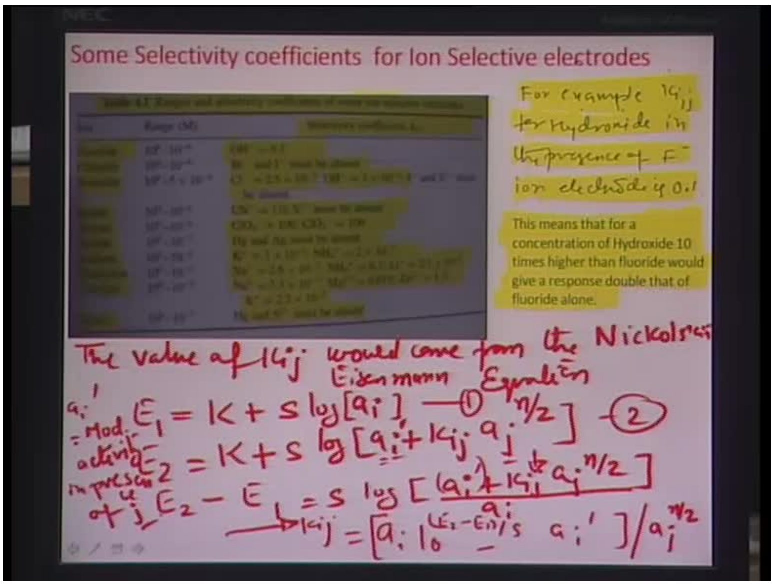

Some Selectivity coefficients for Ion Selective electrodes

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

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

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

Let us also look at one more aspect, how to determine the value of k ij and I would like to do some derivations here. When we were talking about the Nicolskii-Eisenmann equation the value of kij would come from the Nicolskii-Eisenmann equation. Let us suppose, we have certain ion of interest i for which the EMF has been measured using the Nernstian equation as E 1 is equal to K plus Nernstian slope S times of log activity of the primary ion a i. When we add a secondary ions let us say, j with a selectivity coefficient k ij, E 2 here can be represented as K plus S log of a i plus k ij a j to the power of n by z; suppose n and z are of course, the valences on ion i, and ion j respectively.

So, if you just try to calculate k ij here it could come out from subtracting equations 2 from 1 and we can get E 2 minus E 1 is S log of a i plus k ij a j to the power n by z by a i. Here, this is actually the modified activity, let us assume that this modified activity is a i dash; this is no longer a i because a i is the activity of the ion in presence of none other and a i dash is the modified activity of the ion in the presence of the phase j.

If you solve this equation and trying to find out what k ij is from this equation; k ij can be written down as a i times of 10 to the power of E 2 minus E1 divided by S minus a i dash divided by a j to the power of n by z that is what k ij would be in this case; a i dash again I reiterate is actually the modified or corrected activity of the mixed solution. Let me write it down somewhere that in this particular case a ij a i dash is modified activity in presence of ion j.

Since, 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 a methodology for calculating the selectivity coefficient. Now let us do a practical example wherein we have let us say, two participating solutions and we have a data of the EMF from the pure solution as well as the mixed phase, were both the solutions are participating both the ions are participating. We try to calculate what the k ij or the selectivity coefficient would be.

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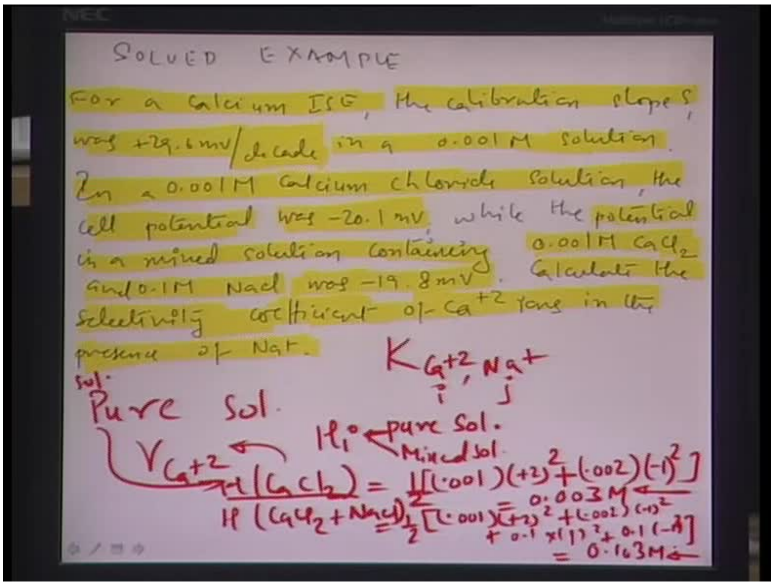

SOLVED EXAMPLE

For a Calcium ISE, the calibration slope S, was +29.6 mV/decade in a 0.001 M solution. In a 0.001M Calcium chloride solution, the cell potential was −20.1 mV while the potential in a mixed solution containing 0.001M $CaCl_2$ and 0.1M 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.

$\gamma_{Ca^{+2}}$

$\mu_i \leftarrow$ pure Sol. / Mixed Sol.

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

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

Let us look at the solved example here. Let us suppose that for calcium ISE for a calcium ion selective electrode the calibration slope S is essentially plus 29.6 milli volts per decade; this word decade essentially means 1 order of concentration. The concentration is changed by 1 order; the log to the base 10 of it would be changed by exactly 1 unit. Therefore S essentially is nothing but, plus 29.6 milli volts; it also makes sense because S is equal to if you look at is the 59 milli volts divide by number of electrons transferred n in this case is 2 because calcium can get oxidized to calcium plus 2 state and therefore, in that case also, the slope is plus 29.6 milli volts.

This is essentially the calibration slope is in a 0.001 molar solution and so in a 0.001 molar calcium chloride solution the cell potential while measuring through the ion selective electrode was measured to be 20.1 milli volts. Now, we mix this calcium chloride solution with Nacl or salt solution in the following ratio and then measure the potential again. The potential in the mixed solution containing 0.001 molar of Cacl 2 and point 1 molar of Nacl was 19.8 milli volts.

The pure solution of calcium chloride with ion selective electrode on calcium measures 0.001 molar and the 1 with mixed solution containing 0.001 molar of calcium chloride and 0.1 molar of Nacl was minus 19.8 milli volts. You have to calculate the selectivity coefficient of Ca plus 2 ion in the presence of Na plus. So, the selectivity of the calcium plus 2 ions in the presence of Na plus has to be calculated.

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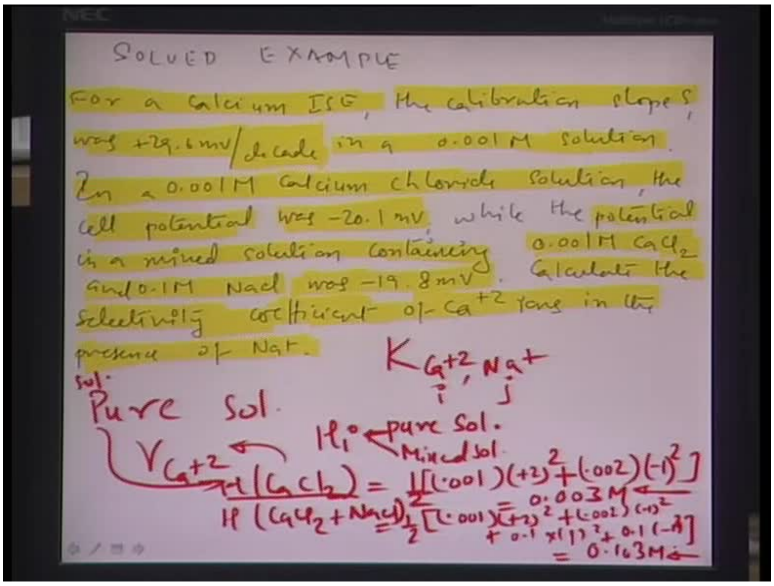

SOLVED EXAMPLE

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

Sol.

Pure Sol.

$\gamma_{Ca^{+2}}$

μ_i ← pure Sol. / Mixed Sol

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

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

In other words, if you look at the ion selective coefficient you are essentially calculating K ca plus 2, Na plus this is the jth ion - the interfering ion, this is the ith ion. How do we calculate it? So to begin with, we have to first calculate the activities of the calcium and sodium ion in the pure solution and the mixed solution.

Let us first do the pure solution case. In the pure solution we had to calculate what gamma Ca plus 2 would be and so for doing that we need an ionic strength, a mean ionic strength, of pure solution and also mixed solution. So, ionic strength of Cacl2 half Ci Zi square Ci here is 0.001 if it is a pure solution times of plus 2 square the charge on the calcium or the valancy on the calcium is plus 2 plus Cacl 2. So there are 2 chlorine atoms per molecule of Cacl 2 and so the chlorine concentration would be exactly double 0.002 molar times of minus 1 square, this comes to be 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 mixed solution, which has Cacl 2 and Nacl both phases. We have half times of and the concentration of Cacl 2 is 0.001 molar as reported in the mixed solution with 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 valancy on the Nacl plus 0.1 times of minus 1 square and this comes out to be effectively equal to 0.103 molar. So 1 mu for Cacl 2 comes out to be 0.003 molar and for a mixed solution the mean ionic strength comes out to be 0.103 molar. After doing this, let us find out that in pure solutions, what the activity coefficient of the Ca plus 2.

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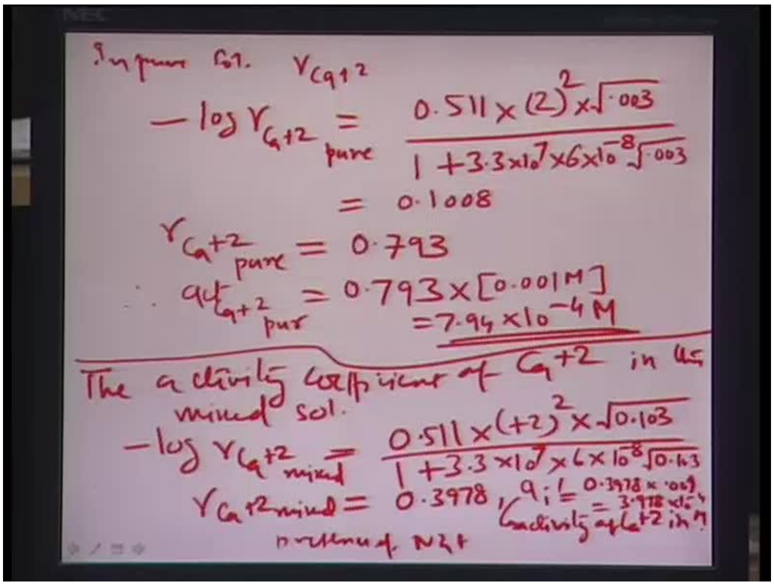

In pure sol. γ_{Ca+2}

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

$$= 0.1008$$

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

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

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

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

$$\gamma_{Ca+2\,mixed} = 0.3978,\quad a_i = 0.3978\times.001 = 3.978\times10^{-4}$$

(activity of Ca+2 in ?)

presence of Na+

In pure solution the activity coefficient of Ca plus 2 can also be represented by the following. Minus log of gamma Ca plus 2, let us indicate this as pure equals 0.511which is the parameter A which we calculated before plus Zi square. In this case, it is plus 2 square the valancy on calcium is plus 2 times of root over the mean ionic strength, which was found out from 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 ions as you can see here in this case, is close 600 pico meters, so it is about 600 pico meters. So 6 10 to the power minus 8 centimeters again I would like to reiterate that all these system of equations is based on CGS units. We need to take the value in centimeters, so 6 to the power of minus 8 is the ion size parameter A in this case types times root of 0.003 the mean ionic strength. So this comes out to be equal to 0.1008.

Essentially taking antilog on both sides the gamma value or the selectivity coefficient of the pure Ca plus 2 comes out to be equal to 0.793 as in this particular case. In pure solution therefore, if we see what is the ionic activity of the calcium plus 2 ions so the a i value for the Eisenmann equation it comes out be equal to act Ca plus 2 pure the gamma Ca plus 2 pure times of the concentration in this case is 0.001 molar. So, it comes out to be 7.94 10 to the power of minus 4 molar, that is what the activity of the pure calcium ions is in a pure solution.

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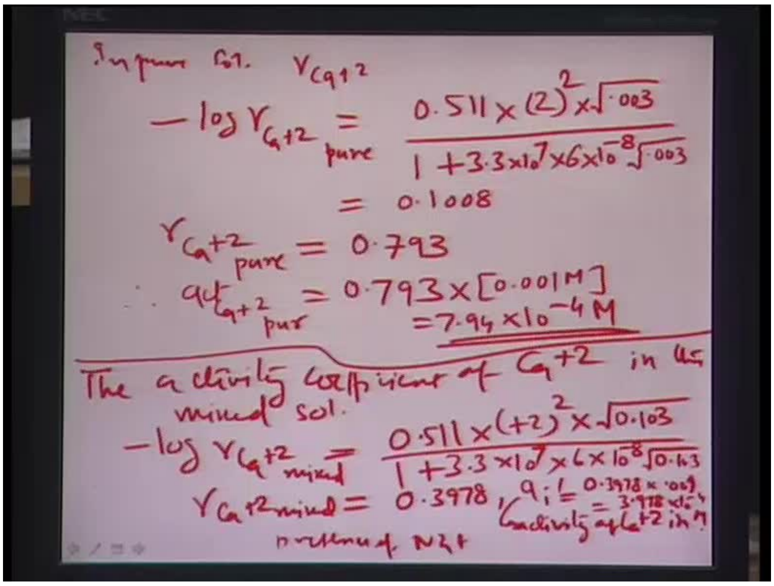

In pure sol. $\gamma_{Ca^{+2}}$

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

$$= 0.1008$$

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

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

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 presence of Na+)

Let us simultaneously find out, what is a i dash. That means, the activity of the calcium plus 2 ions in the presence of Na plus. In order to do that in the second phase of this question we need to actually see, what is the activity coefficient for Ca in the mixed solution? We find out the activity coefficient of Ca plus 2 in the mixed solution. We have in the mixed solution minus log of gamma Ca plus 2 and let us call this phase mixed phase equals 0.511 which is the a parameter times 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 you remember, divided by 1 plus 3.3 10 to the power of 7 which is the B parameter times of again the calcium ion of course, has the ion size parameter of 600 pico meters which we just deciphered a moment back last slide was 6 into 10 to the power minus 8 times of root of 0.103.

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 or the a i dash value that means, the activity of Ca plus 2 in presence of Na plus that comes out to be equal to essentially 0.3978 times 0.001 which is also the molarity of the Cacl 2 in the mixed solution and that is 3.987 into 10 to the power of minus 4 molar. So that is what the mixed activity or activity of Ca plus 2 phases in the mixed solution.

Going to the second part of the problem, let us find out, what is the a j value; that is the j in this case being the sodium plus ion or Na plus ion the a j value essentially is the activity of the Na plus or the presence of Ca plus 2, so we calculate that here.

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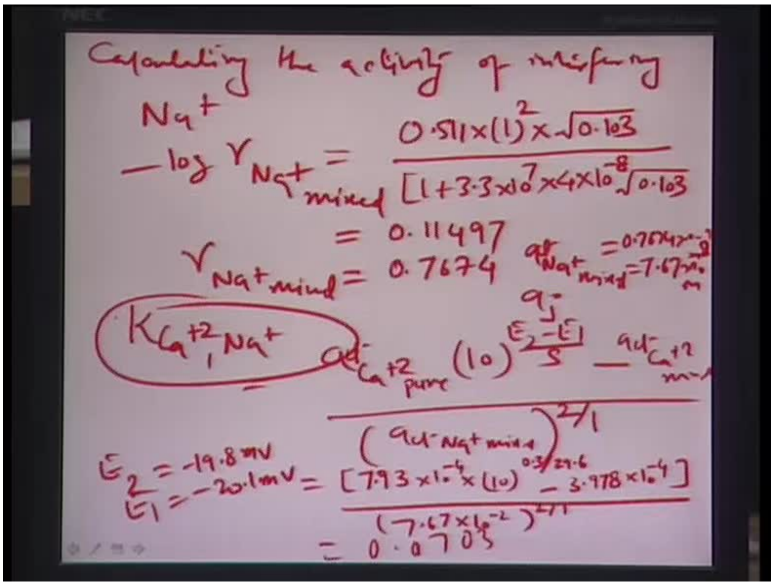

Calculating the activity of interfering Na^+

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

$$= 0.11497$$

$$\gamma_{Na^+_{mixed}} = 0.7674 \qquad a'_{Na^+_{mixed}} = 0.7674\times 10^{-1} = 7.67\times10^{-2}\ M$$

$$\boxed{K_{Ca^{+2},Na^+}} = \frac{a'_{Ca^{+2}_{pure}}(10)^{\frac{E_2-E_1}{S}} - a'_{Ca^{+2}_{mixed}}}{(\overset{a_j}{a'_{Na^+_{mixed}}})^{2/1}}$$

$$E_2 = -19.8\ mV \qquad E_1 = -20.1\ mV$$

$$= \frac{[7.93\times10^{-4}\times(10)^{0.3/29.6} - 3.978\times10^{-4}]}{(7.67\times10^{-2})^{2/1}}$$

$$= 0.0703$$

Calculating in the next phase, the activity of the interfering ion here the a i dash, a i, a j are all according to the Nicolskii-Eisenmann equation, which we had discussed just about 2 3 slides back. Essentially, the interfering ion here is Na plus so for the Na plus we have minus log gamma Na plus in the we call it mixed again because the Na plus is present only in the mixed solution is equal to 0.511 A parameter times of Z square. Z in this case is plus 1 because Na has a univalent ion, so Na plus is a univalent so plus 1 square times of root of the mu which is again it does not get altered, mean ionic remains 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 minus 7 which is the B parameter times of the value of Na or the ion size parameter of Na which is about 400 pico meters from the table as we had done before. So, this is 4 10 to the power minus 8 centimeters again the CGS units have to be used root over 0.103 and this comes out to be equal to 0.11497.

Therefore, the gamma Na plus in the mixed phase or 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 Na plus in the mixed phase comes out to be 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 is, so this is corresponding to also a j.

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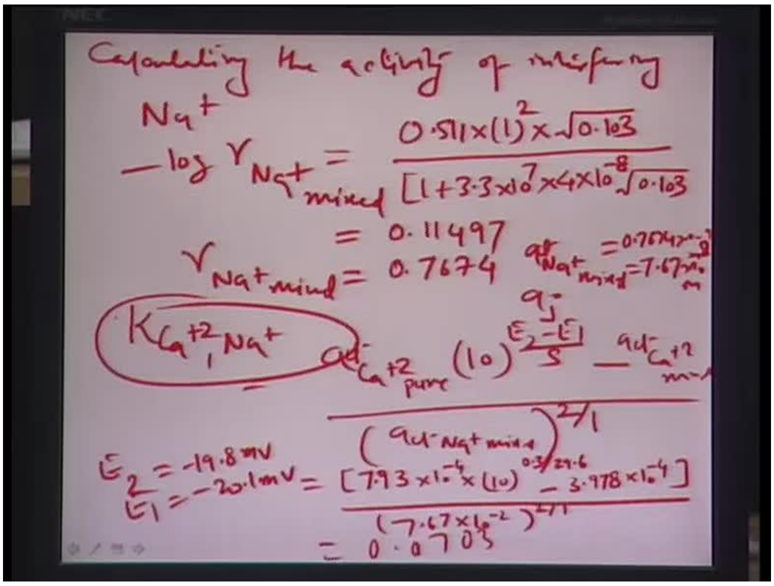

Calculating the activity of interfering Na^+

$$-\log \gamma_{Na^+ \text{mixed}} = \frac{0.511 \times (1)^2 \times \sqrt{0.103}}{[1 + 3.3\times10^7 \times 4\times10^{-8}\sqrt{0.103}}$$

$$= 0.11497$$

$$\gamma_{Na^+ \text{mixed}} = 0.7674 \qquad a_{Na^+ \text{mixed}} = 0.7674\times10^{-1} = 7.67\times10^{-2}\ M$$

a_j

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

$E_2 = -19.8$ mV

$E_1 = -20.1$ mV

$$= \frac{[7.93\times10^{-4}\times(10)^{0.3/29.6} - 3.978\times10^{-4}]}{(7.67\times10^{-2})^{2/1}}$$

$$= 0.0705$$

We have pretty much everything which we need for Nicolskii-Eisenmann equation solution and we need to find out what the ion selectivity coefficient of K Ca plus 2 is over Na plus 2 in the mixed phase and that can come out by the equation a i 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 E 2 minus E 1 by S. If you remember from the question earlier, the E 2 was given as minus 19.8 milli volts that is the potential generated by measurement along the mixed phase or the mixed solution and E 1 the potential on the pure solution was given as minus 20.1 milli volts.

E 2 minus E 1 by S really is nothing but, 0.3 divided by 29.6. Therefore, this 10 to the power E 2 minus E 1 by S minus a i 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 a j 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 valancy of Ca primary ion of interest and z is the valancy of the secondary ion or the interfering ion as 1 as in case of Na plus.

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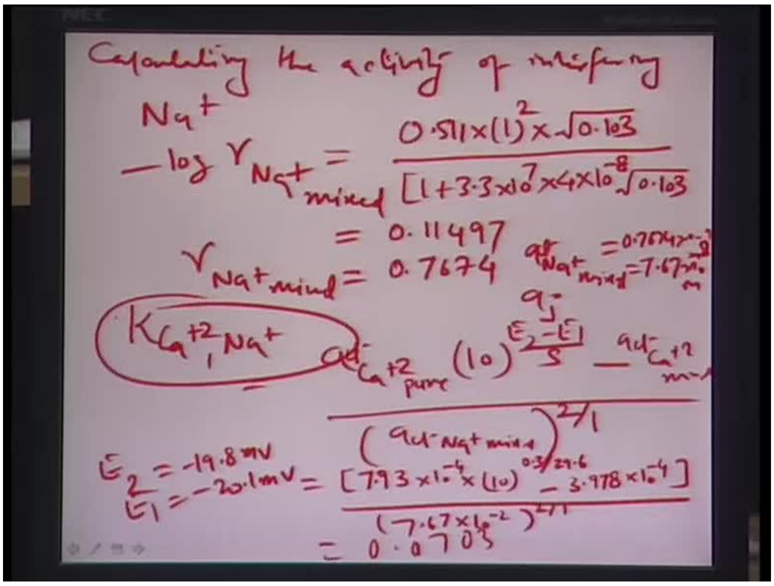

Calculating the activity of interfering Na^+

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

$$= 0.11497$$

$$\gamma_{Na^+_{mixed}} = 0.7674 \qquad a_{Na^+_{mixed}} = 7.67\times10^{-2}\ M$$

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

$E_2 = -19.8$ mV

$E_1 = -20.1$ mV

$$= \frac{[7.93\times10^{-4}\times(10)^{0.3/29.6} - 3.978\times10^{-4}]}{(7.67\times10^{-2})^{2/1}}$$

$$= 0.0703$$

So, if you put back all the values here it comes out to be equal to 7.93 10 to the power of minus 4 times 10 to the power of and you calculate this as 0.3 divided by 29.6 milli volts minus 3.978 10 to the power of minus 4, these values have been all calculated earlier, if you may recall divided by this 7.67 10 to the power of minus 2 times to the power of 2 by 1 that is 2 this comes out to be equal to 0.0703. So that is what the K Ca plus 2 in the presence of the interfering ion Na plus is going to be.

What really it means is that, the solution containing almost 14 times as much Na plus as Ca plus 2 would give a response to which is double that of the value for Ca plus 2 ions alone. Definitely, Na plus ion is weakly interfering ion to Ca plus 2. In conclusion, what I would like to ascertain here is that in these kinds 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 a primary interest and this is definitely very helpful for designing ion selective electrodes.

So, we are almost towards the end of this lecture and I would like to discuss again what we would take up in the next lecture. We have now by and large seen detailed derivations about ionic activity, understood and realized the importance of how it is helpful in designing ion selective electrodes and also how we can predict the EMF of a solution which has all these mixed phase ions of different kind with some interfering some primary ions of interest.

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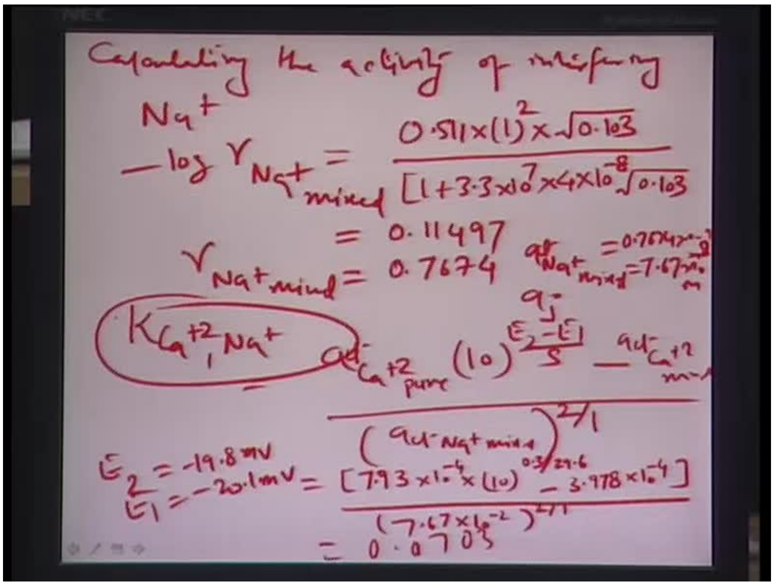

Calculating the activity of interfering

Na^+

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

$$= 0.11497$$

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

$$a_j$$

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

$E_2 = -19.8$ mV

$E_1 = -20.1$ mV

$$= \frac{[7.93\times10^{-4}\times(10)^{0.3/29.6} - 3.978\times10^{-4}]}{(7.67\times10^{-2})^{2/1}}$$

$$= 0.0703$$

Now, coming to some physically realizable electrodes etcetera, the natural question is that can we really look at some of the sensors more closely and how the mechanisms helps to sense things like gases or things like certain metabolites or chemicals. These sensors are often on used in medical diagnostics area where problems related to increase in urea within the blood or increase in blood glucose etcetera are quickly recorded and sent almost real time investigation is sometime done on the bedside as we have been talking out in our earlier lectures before.

In the next lecture, I would like to cover more or less some details about, what is that interface of some of these sensors with the different metabolites of interest related to human body, human blood or some other gases which may be effective for designing a gas sensor eventually. Then, we would like to look at how we can further miniaturize them to have an electrochemical response and understand how in a MEMS way in a micro engineering manner or using micro engineering tools we could develop something sensitive to detect and pickup analyses of interest. So, I would like to close this lecture with this.

Thank you