Bio-Microeletromechanical Systems

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Module No. # 01

Lecture No. # 08

Welcome back to lecture number eight of this particular course. Last time, we saw how to do the coordinate transformation and let me just take you through the same. Before that, we try to get into this ionic activity and try to derive the activity co-efficient using the Debye-Huckel equation.

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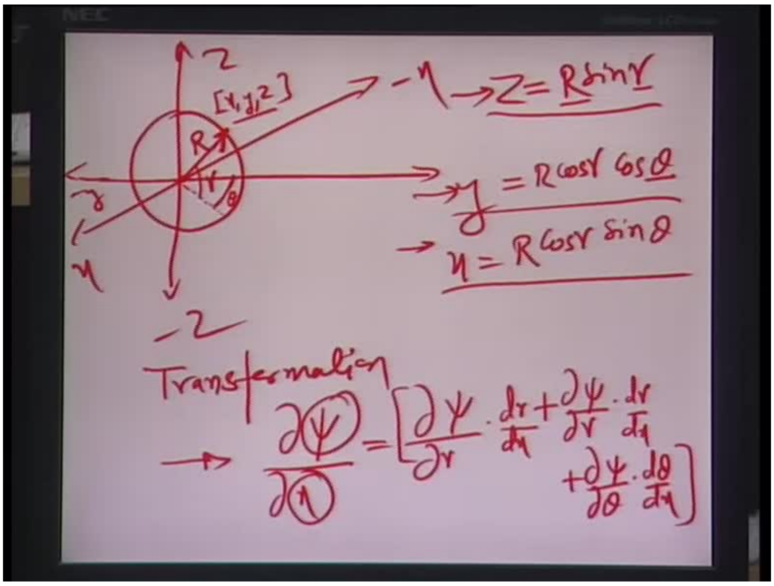

We just about started on that after essentially completing the Gran plot scheme of calibration and measurement of electrode. The coordinate transformation was needed because we were trying to illustrate or we were trying to find out mathematically the potential function. So, we use the Poisson’s equation which is the spatial derivate of the potential function and equated that to the charge density, 4 pi rho by d. We also figured out that because we were talking about spherical central charge of interest and ion cloud around it. We would have to deal eventually with the spherically symmetric situation that will make our life easier. Therefore, we made a coordinate transformation of Cartesian to spherical.

In this case, we illustrated how we can find out this x y z, the point on top of this radius vector with respect to R gamma and theta, gamma being the angle between the projections of the radius in the x y plane. Theta is the angle between one of the axes, in this case, the y axis, with this projection vector on the x y plane.

To do the coordinate transformation, I would expect the students to actually go do this as a part of the homework assignment may be eventually given. If we consider the whole distribution and also consider spherical symmetry that means no variation whatsoever with gamma or theta, so, spherical symmetry as if these potential functions are like shells around the small positive charge of interest.

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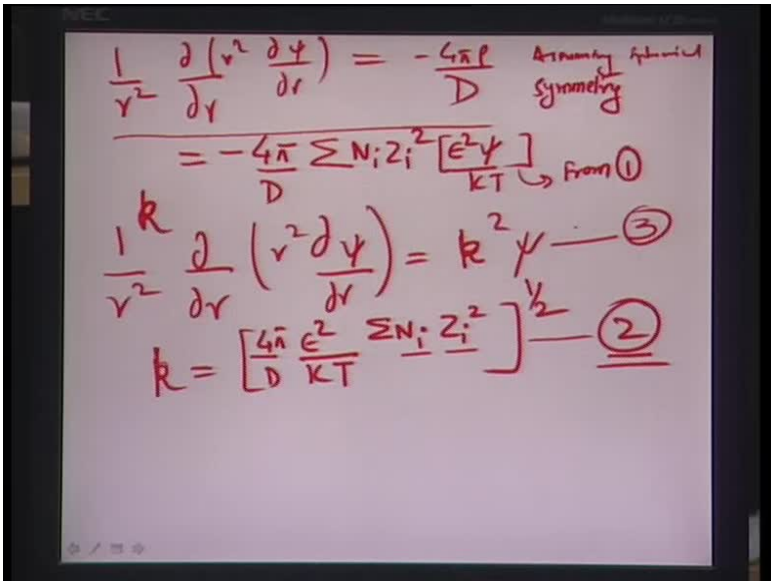

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) = -\frac{4\pi\rho}{D}$$

Assuming spherical symmetry

$$= -\frac{4\pi}{D}\sum N_i z_i^2\left[\frac{\epsilon^2\psi}{KT}\right] \hookrightarrow \text{From } ①$$

$${}^{k}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) = k^2\psi \text{ --- } ③$$

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

In that case, the final equation boils down to 1 by r square partial of partial with respect d r of r square partial of y with respect to r. This can be equated to minus 4 pi rho by D. That is how the Poisson’s equation can be written down assuming spherical symmetry. So, the potential function’s variation is purely with respect to the radius vector r in that case. This can further be expanded into by putting the value of rho that we obtained earlier in terms of the subscript i and the total number of charges on the point A as minus 4 pi by D N i Z i square epsilon square phi by KT. This is essentially from 1. We had assumed this equation number 1 in the earlier presentation.

Now, let us make some presumptions here. We just for the sake of convenience, assume a factor K. This is actually different from the Boltzmann's constant K. Let us see in order to just make a little more simplified without any problem, let us consider this to be small k. We can rewrite this equation as 1 by r square d by d r, r square d phi d r to be equal to small k square phi. What is k square in that case? k is essentially a parameter, which is equal to minus 4 pi or it is equal to 4 pi by D epsilon square by KT, where K in this case is the Boltzmann's constant, sigma N i Z i square to the power half. Let us actually write this as equation number 2. This is very important, because later on we have to write the final formulation in terms of the subscript i and various other parameters which are included in this small k concept. Let us call this equation 3.

If you go through p d partial differential equations again any graduate program on them, there are generalized solutions for finding out the solution for certain kind of p ds. In this case, generalized solution that one can think of for equation 3 comes out to be equal to phi equals A e to the power of minus k r by r plus A dash e to the power of k r by r. A and A dash are constants. We should need to know certain unknown, r of course, is the radius vector and k as we know is given by equation 2 here.

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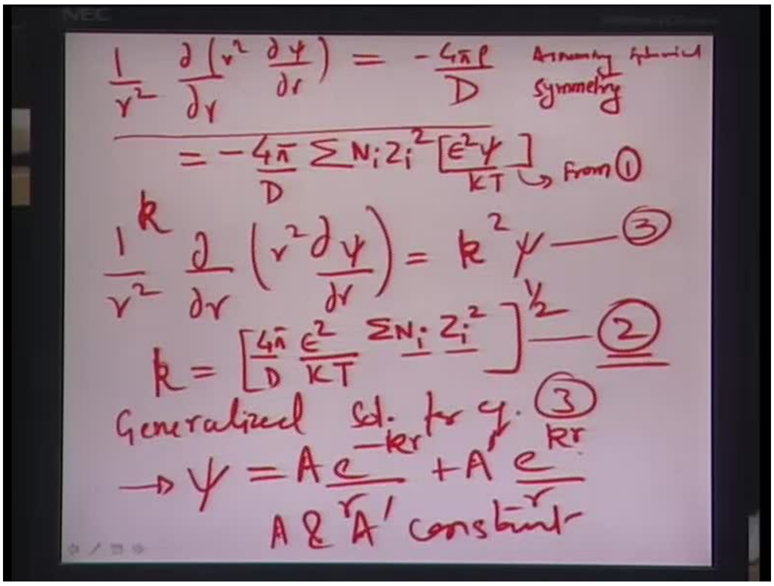

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = -\frac{4\pi\rho}{D}$$ Assuming spherical symmetry

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

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = k^2\psi \quad \text{— ③}$$

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

Generalized sol. for eq. ③

$$\rightarrow \psi = A\frac{e^{-kr}}{r} + A'\frac{e^{kr}}{r}$$

A & A' constant

So, one way of checking back whether this is going to work or not is to put the value of phi in equation 3 and see whether you have equality on both sides. If we put this root and try to the evaluate the various aspects of the behavior of potential function that means what we know as boundary conditions of the potential function, we would be able to estimate this co-efficients, A and A dash.

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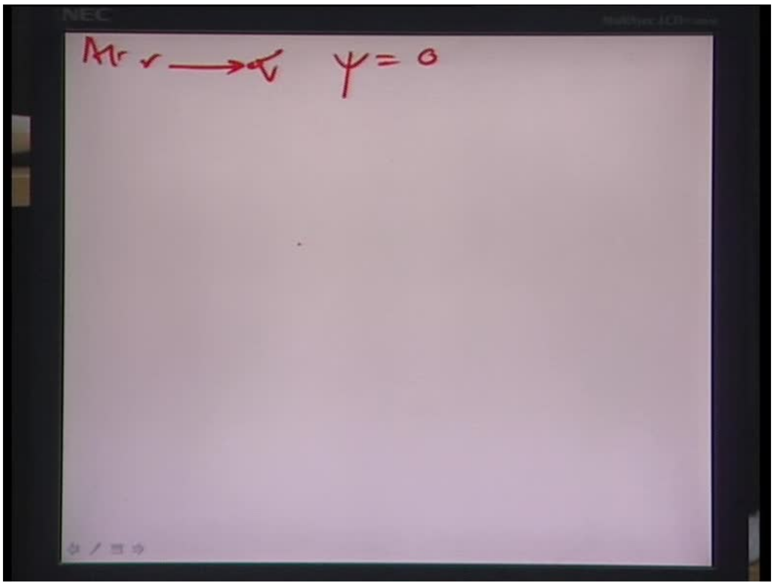

At $r \rightarrow \infty$ $\psi = 0$

Let us look at it how. As we know that at r tending to infinity, the potential function phi would be also equal to zero. That is what the basic premise was, when we were talking about central charge distribution and ion cloud that the potential generating from this small positive ion of interest at a distance which is infinitely spaced would be zero. There is no potential at infinity.

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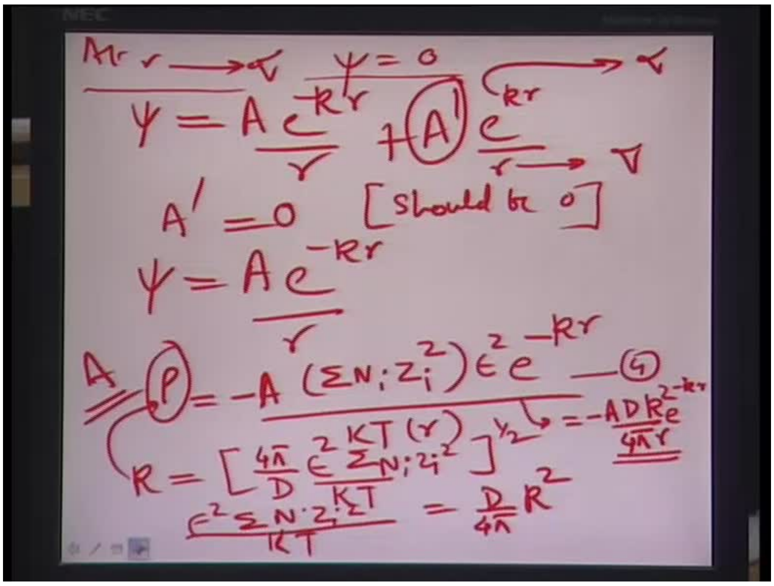

At $r \rightarrow \infty$ $\psi = 0$

$$\psi = A\frac{e^{-\kappa r}}{r} + A'\frac{e^{\kappa r}}{r} \rightarrow \infty$$

$A' = 0$ [Should be 0]

$$\psi = A\frac{e^{-\kappa r}}{r}$$

$$\rho = -A\frac{(\Sigma N_i z_i^2)\epsilon^2 e^{-\kappa r}}{kT(r)} \quad (4) \quad = -\frac{AD\kappa^2 e^{-\kappa r}}{4\pi r}$$

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

$$\frac{\epsilon^2 \Sigma N_i z_i^2}{kT} = \frac{D}{4\pi}\kappa^2$$

Therefore, if you assume phi to be zero at r equal to infinity and if you know from earlier that the equation for phi is A e to the power of minus k r by r plus A dash e to the power of k r by r, then the only way you can have this condition- r equal to infinity phi equal to zero validated is by assuming that A dash is equal to zero for obvious reasons. Because if r is infinity, then in that case this particular term here, e to the power k r should also go to infinity and r being infinity, the only way to avoid this situation is by assuming a zero co-efficient so that there is a validation. Therefore, really phi is represented as A e to the power of minus k r by r. As we know from earlier that the rho, the charge density is also minus A times of sigma N i Z i square epsilon square e to the power of minus k r by K T times of r.

This is same as writing minus sigma N i Z i square E square phi by K T, phi being e to the power of minus k r by r. We have just made a slight rearrangement here for the charge density. If we look at the equation number 2 that we have done before, in terms of k, how we can represent this whole expression. Then from there, we can easily get that k here, if you look at has been represented as 4 pi by D epsilon square Boltzmann's constant K times of T sigma N i Z i square to the power of half. We can do a little bit of manipulation here so that we can represent this whole term in terms of k. From here, we can also have an expression wherein the epsilon square sigma N i Z i square by K T term, where K here is K is Boltzmann's constant represented as D by 4 pi small k square. If I substitute that back into this equation 4 here and the final equation that I get is basically minus A times of D k square by 4 pi e to the power of minus k r and of course, there is a r term in the denominator, so, it is basically A k square D and since this particular term can be represented as minus A D k square e to the power of minus k r divided by 4 pi r.

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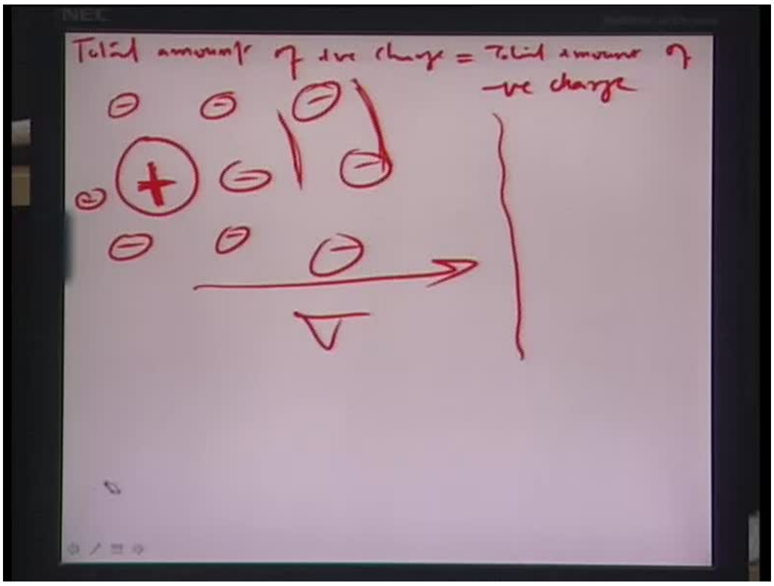

Total amount of +ve charge = Total amount of −ve charge

This is an important aspect, because this is what the charge density at point A is. We will like to have a look at what is the corresponding counter ion cloud charge density. For doing that, as we are aware that the principle of electro neutrality is always to be followed and by that principle we know that the total amount of positive charge in a sense would equalize the total amount of negative charge.

This is very interesting situation because we have a case where we have a positive charge here and there are several minus charges or negative charges in the counter ion clouds here exactly. So, the total charge in the ionic atmosphere let us say all the way up to infinity here, it is going up to infinity, there are charges here, there are charges here, there is a whole bunch of these counter ion charges assuming a single positive of charge all the way up to infinity which would totally be able to balance in this particular charge. If you assume that and if we try to find out what is really this charge density of the counter ion cloud and equate that to just the negative magnitude of the positive charge here, we should be able to get an equality between the two.

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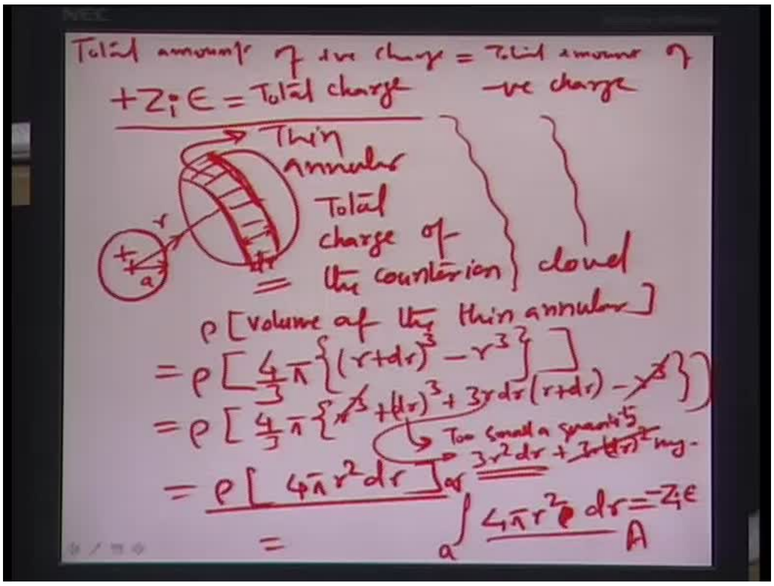

Total amount of +ve charge = Total amount of −ve charge

$+Z_i\epsilon$ = Total charge

Thin Annular

Total charge of the counterion cloud

= ρ[volume of the thin annular]

$= \rho\left[\frac{4}{3}\pi\{(r+dr)^3 - r^3\}\right]$

$= \rho\left[\frac{4}{3}\pi\{\cancel{r^3} + (dr)^3 + 3r\,dr(r+dr) - \cancel{r^3}\}\right]$

Too small a quantity

$\underline{\underline{3r^2dr}} + \cancel{3r(dr)^2}$ neg.

$= \underline{\rho[4\pi r^2 dr]}$ or

$= \int_a \underline{4\pi r^2 \rho\, dr} = -Z_i\epsilon$

A

Let us try and do that and then with the charge density that we had figured out in our earlier slide, we will try to find out what the coefficient A would be and this is of immense utility for us as we will see later. All these ionic activity and ion selective electrodes do depend a lot on how this particular behavior of surrounding ions would be effecting the electrical contribution of the particular ion of interest in each case. In our case, it is positive ion.

Let us assume the central charge to have plus Z i epsilon as the total charge. If I have a positive ion here and this has a radius a, which is very close by here. We assume that there is an ion cloud which extends all the way up to infinity, but then at a distance r from the center, we are trying to the see what is the charge density in a thin shell of the counter ion clouds.

Let us assume that thickness of this shell is as small as an infinitesimally small value of the radius function r here as d r. So, the total charge of the counter ion cloud would be represented as the charge density times the volume of this thin annular, assuming this is a thin spherical annular. So, we need to find out what is the total charge stored in this spherical annular by looking at this volume here. We get this as rho times the volume of annular thin which is 4 by 3 pi r plus d r cube minus r cube. We assume that we are trying to calculate the volume of this thin annular here.

The radius vector all the way up to here is r plus d r, here it is r. So, you are trying to create volume difference. Let us try to look at what this volume would be like, it is essentially 4 by 3 pi and then we have r cube plus d r cube plus 3 r d r times of r plus d r minus r cube. This gets canceled away; this is too small a quantity and if you look at this quantity here, it is 3 r square d r plus 3 r d r square, we assume d r to be so small that even this is neglected.

We are left with only 4 pi r square d r as the elemental volume here in this particular annular. Therefore, if you want to calculate the total charge in this thin annular, it would be total charge of counter ion cloud. So, we can actually give a boundary condition here as if the density has to be calculated from the radius of the basic ion A all the way to infinity of this expression 4 pi r square rho d r. This is nothing but an integration of the surrounding ion density or ionic concentration. What this should be equal to really? As I told before that for the principle of electron neutrality, this should be equal to the negative of the charge as the charge of the primary ion of interest which is the positive charge.

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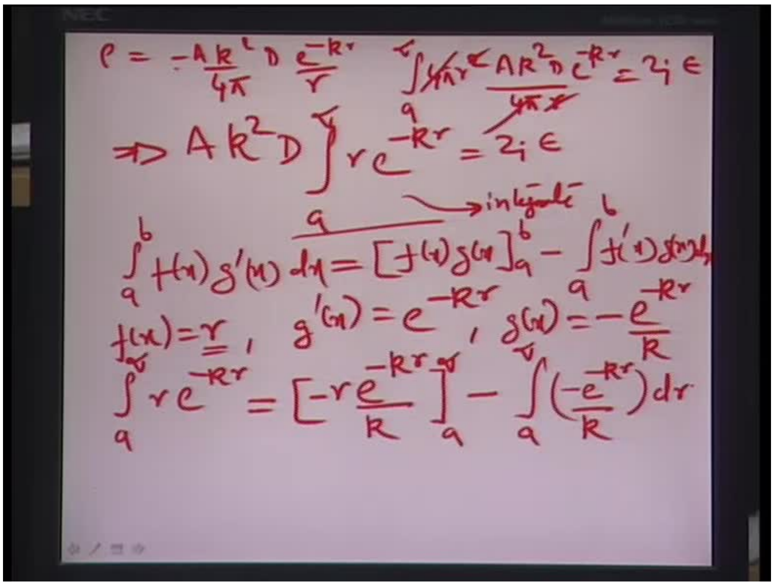

$$\rho = -\frac{Ak^2}{4\pi} D \frac{e^{-kr}}{r} \qquad \int_a^\infty \cancel{4\pi} r^{\cancel{2}} \frac{Ak^2 D e^{-kr}}{\cancel{4\pi}\,\cancel{r}} = z_i e$$

$$\Rightarrow A k^2 D \int_a^\infty r e^{-kr} = z_i e$$

$$\int_a^b f(x) g'(x)\,dx = [f(x) g(x)]_a^b - \int_a^b f'(x) g(x)\,dx$$

$$f(x) = r, \quad g'(x) = e^{-kr}, \quad g(x) = -\frac{e^{-kr}}{k}$$

$$\int_a^\infty r e^{-kr} = \left[-r\frac{e^{-kr}}{k}\right]_a^\infty - \int_a^\infty \left(-\frac{e^{-kr}}{k}\right) dr$$

So, essentially from this equation, we should be able to get some information about the parameter A as we had actually defined before while calculating the density rho. Let us look at how we do that: rho from the earlier equation had come out to be minus A k square by 4 pi, this k here is small k- should not confuse, both are different- times of D dielectric constant times of e to the power of minus k r by r. That is what rho is. We are calculating an integral from a to infinity of 4 pi r square A times of small k square by 4 pi r D e to the power of minus k r - this is equated to Z i times of epsilon for being electrically neutral or in the case of electro neutrality. Mind you that this being negative sign, the negative sign on the right cancels because of that.

So, let us actually try to integrate this and find out what comes. This 4 pi goes away, that is the first power in a r which is retained here and what we are left with is an integral A k square D integral a to infinity r e to the power of minus k r equals to Z i epsilon. We will like to integrate this by parts. If we integrate them by parts between a and b, f x g dash x d x is actually equal to f x g x from a to b minus integral a to b f dash x g x e x. I just want to reiterate what integral by parts is, here f x is equal to A, f x here is equal to r. The g x here is equal to e to the power of minus k r. In this, the g dash x is equal to e to the power of minus k r. Therefore, g x becomes minus e to the power of minus k r by k. That is what g x becomes. Therefore, when we are trying to calculate integral a to infinity r e to the power of minus k r, we are doing minus r e to the power of minus k r by k f x g x term between a and infinity, b in this case is infinity minus integral a to infinity f dash x, which is in this case 1 because of f x is r , f dash is nothing but d by d r of the function r times of g x, which is minus e to the power of minus k r by k d r.

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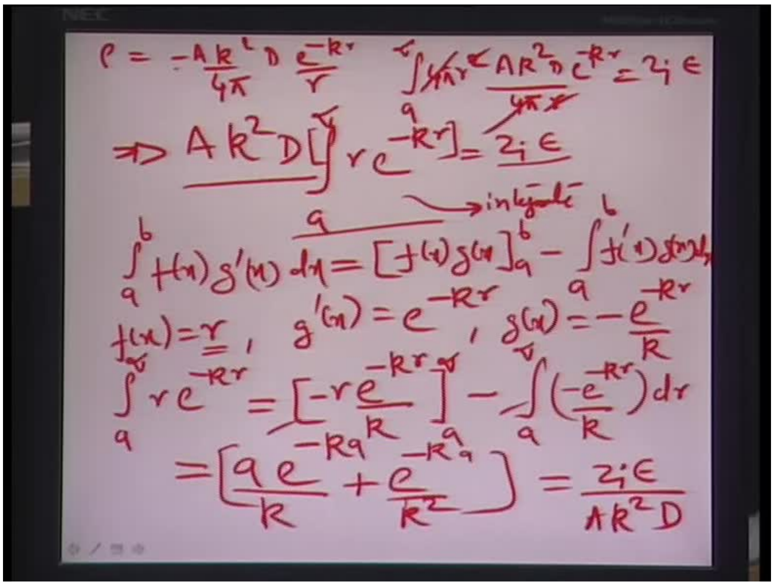

$$\rho = -\frac{Ak^2D}{4\pi}\frac{e^{-kr}}{r} \qquad \int_a^\infty \cancel{4\pi r^2}\,\frac{Ak^2D}{\cancel{4\pi r}}e^{-kr} = Z_i\epsilon$$

$$\Rightarrow \underline{Ak^2D}\left[\int_a^\infty re^{-kr}\right] = \underline{Z_i\epsilon}$$

integrate

$$\int_a^b f(x)g'(x)\,dx = [f(x)g(x)]_a^b - \int_a^b f'(x)g(x)\,dx$$

$$f(x) = \underline{\underline{r}}, \quad g'(x) = e^{-kr}, \quad g(x) = -\frac{e^{-kr}}{k}$$

$$\int_a^\infty re^{-kr} = \left[-r\frac{e^{-kr}}{k}\right]_a^\infty - \int_a^\infty\left(-\frac{e^{-kr}}{k}\right)dr$$

$$= \left[\frac{ae^{-ka}}{k} + \frac{e^{-ka}}{k^2}\right] = \frac{Z_i\epsilon}{Ak^2D}$$

That is what this integral would be eventually looking like. On solving this equation, we get the final value here as, a e to the power of minus k a by k plus e to the power of minus k a by k square - that is what the final integral would look like after we put the value of r between a and infinity and evaluate these term 1 and term 2 here in this particular equation. That is what Z i E would really be.

Starting from here, we should get an idea of what a would be, because a is in the potential term and from the differential equation a is also unknown so far and we need to estimate the value of capital A. This would be the only method of doing that. Let us look at by solving what the value would come out to be equal to. We just rewrite this particular value of A k square D into the integral which we had just tried to find out is Z i E, so, this becomes Z i E by A k square D.

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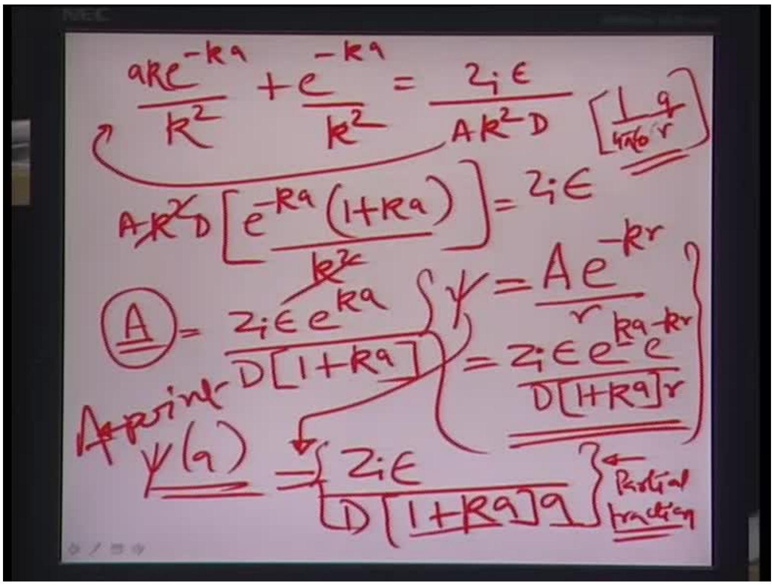

$$\frac{ake^{-ka}}{k^2} + \frac{e^{-ka}}{k^2} = \frac{Z_i \epsilon}{Ak^2 D} \qquad \left[\frac{1}{4\pi\epsilon_0}\frac{q}{r}\right]$$

$$A\cancel{k^2}D\left[\frac{e^{-ka}(1+ka)}{\cancel{k^2}}\right] = Z_i \epsilon$$

$$\underline{A} = \frac{Z_i \epsilon e^{ka}}{D[1+ka]}$$

$$\psi = \frac{Ae^{-kr}}{r} = \frac{Z_i \epsilon e^{ka} e^{-kr}}{D[1+ka]r}$$

A point

$$\psi(a) = \left\{\frac{Z_i \epsilon}{D[1+ka]a}\right\}$$

Partial fraction

We take this equation to the next page. We have on one side a e to the power of minus k a by k plus e to the power of minus k a by k square and that is equated to Z i E by A k square D. Let us take this term right, we are left with A k square D times of - If I try to multiply this term by k above and below so that there is a common denominator, we are left with e to the power of minus k a times of 1 plus k a by k square is Z i times of epsilon. These two go away and we are left with an expression A equals Z i epsilon e to the power of k a by D 1 plus k a.

That is what the value of A is, the co-efficient A is. Simultaneously, if you look at what phi is, phi was represented as A e to the power of minus k r by r. Substituting the value here, we are left with Z i epsilon e to the power of k a e to the power of minus k r times divided by D 1 plus k a times of r. That is what the potential function phi at that particular point is. So, now we have pretty much everything known. We know what k is. We still do not know what a is. This a is also known as the ion size parameter as we look at in the next slide.

The first thing which comes to our mind is let us really find out what psi at a is, that is essentially what the potential function at the point A really was. If I put the value of A in this particular equation here, we are left with Z i E epsilon divided by D 1 plus k a times of a, as these two terms, k a and for r is equal to a, they cancel out. So, we are left with Z i epsilon by D times of 1 plus k a times of a. This gives us an interesting observation.

We can try to independently make these two co-efficients on two different terms on the denominator or we can to try to solve this particular equation using partial fraction concept to interpret about what is the contribution of the ion and the potential and what is the contribution of the surrounding and atmosphere because potential as you know is nothing but 1 by 4 pi epsilon naught some charge contribution let us say q divided by the radius of the distance of a point from that particular charge. In this case, the distance that we have considering is a, so let us actually split it using partial fraction.

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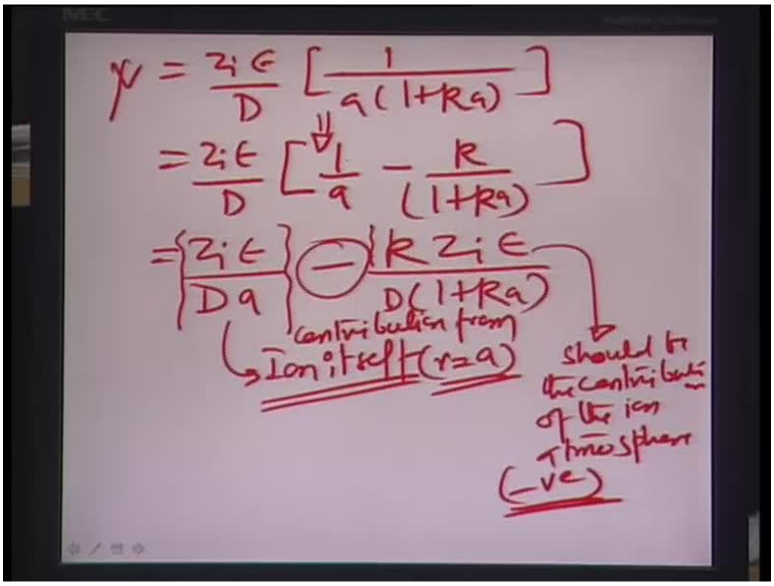

$$\psi = \frac{z_i \epsilon}{D}\left[\frac{1}{a(1+Ka)}\right]$$

$$= \frac{z_i \epsilon}{D}\left[\frac{1}{a} - \frac{K}{(1+Ka)}\right]$$

$$= \left\{\frac{z_i \epsilon}{Da}\right\} \boxed{-} \left\{\frac{K z_i \epsilon}{D(1+Ka)}\right\}$$

contribution from Ion itself (r = a)

should be the contribution of the ion atmosphere (–ve)

If you try to do that, the phi value can be represented as 1 by a 1 plus k a can be written in terms of partial fraction as 1 by a minus k times of 1 plus k a. Let us compute this. If you make this, the denominator will come out to be a times of 1 plus k a and 1 plus k a will be k minus k times of a so that essentially this is 1 by a in to 1 plus k a. This is the correct partial fraction for this expression on the top and let us split it up in to two different terms Z i by D times of a minus k divided by D times of 1 plus k a times of Z i E. What we are sure about one thing is that this probably corresponds to the contribution from the ion itself as it corresponds to an r value equal to a as we had investigated before the radius value equal to a and this should be - because even it is negative as you can see here, should be the contribution of the ion atmosphere. This is a very important fact that this is a negative ion atmosphere, because central ion was positive. Therefore, the contribution to the potential function by this particular term here is also negative.

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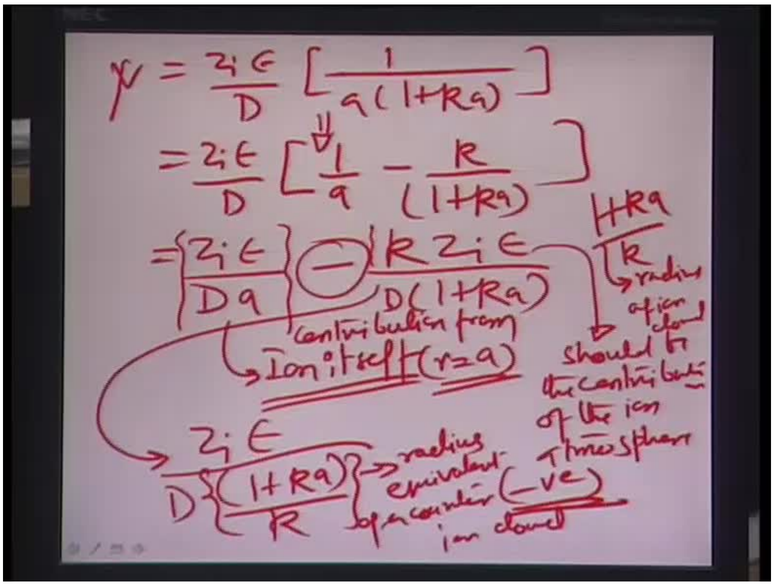

A very important factor here then is that the final potential function is not only because of the charge of interest but also because of the surrounding counter ion cloud or the counter ion charge which is surrounding it. Therefore, if we try to estimate what is an average radius or what is an equivalent radius of such counter ionic cloud, I could write this down very well as Z i E by D times of 1 plus k a by k. This is the radius equivalent of a counter ion cloud. This is the radius equivalent of a counter ion cloud and which might mean that 1 plus k a by k is the radius of ion cloud.

Now, let us go to another very important aspect. How we can correlate all this information to the activity of the particular ion of interest, which is the positive ion in this case? Basically, we would now like to find out how whatever we have done so far is related to the activity of an ion of interest. For that, there has to be some kind of a relationship in terms of the amount of work that is done for bringing small amount of the counter ion cloud from infinity into the center of the counter ion cloud and try to equate that to delta G equation, Gibb’s free energy equation. This will be clear in a little bit when I demonstrate that part.

Let us study first that what would be the free energy involved in all this process where the ions come from infinity, they form a counter ion of minus Z i E around the main ion of interest which is plus Z i E; how all that happens, the amount of maximum work done which is also equal to the free energy of the system, how that can be defined in terms of the ionic concentration.

As we know from the Van’t Hoff equation while doing electrochemical cells, we found out that the amount of free energy of such a self-organizing system would be given by the equation, delta G equal to delta G naught plus r times t natural log of activity of the ion which is gamma i x i; if you remember when we talked about the ionic activity and in fact when we were discussing the electrochemical cell, we considered that there is a lot of high ionic background and therefore, there is only one specific ion of interest and so the activity co-efficient gamma is one in that case. But in our case here, the activity co-efficient was a function of a concentration here though the activity is - because of the several interacting ions that are present in the solution of finite value, gamma i into the concentration of the i th species.

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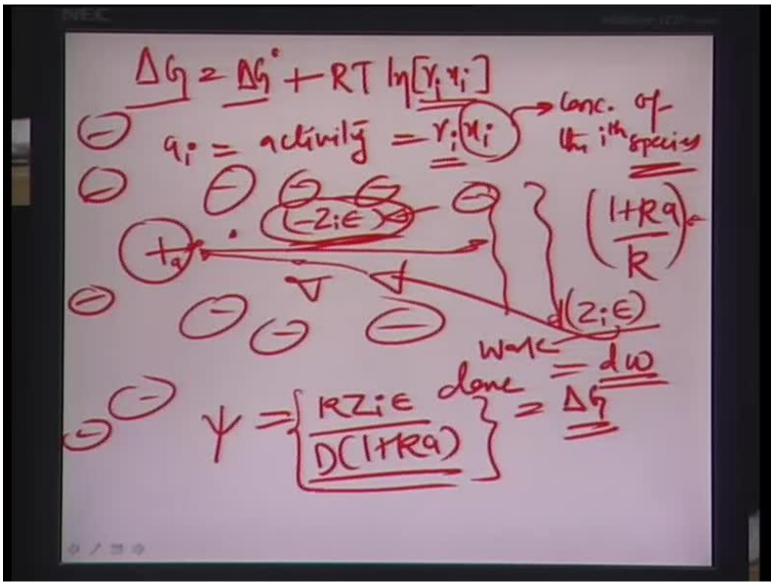

So, we do get a relationship between the free energy associated with this dynamics that is going on around the positive ion and the activity of the particular species of interest. Let us see what would be needed to bring a few moles of the counter ion cloud from infinity into such a cloud. Let us say you have a positive ion here; this is the infinite plane probably and there is a bunch of counter ion clouds which are surrounding at all directions and you have this counter ionic radius that is given from the earlier equation by this factor 1 plus k a by k as we did in the earlier equation.

Now all set and done. Let us say this kind of charge distribution is existing and you want to bring some charge, some elemental charge, let us also assume this is minus Z i epsilon; we assume that this total counter ionic charge is minus Z i epsilon. We made this presumption while deriving this ionic radius formulation of the cloud. We assume that a very small amount of this charge, d Z i epsilon is being brought in this counter ion cloud.

So, the amount of work that would be done for such a small charge to get into the counter ion cloud of value Z i E may be at a point where the potential is also defined by the formulation, K Z i epsilon by D 1 plus k a, so, if you may remember this was the contribution of the potential from the negative ion. If you have a potential function somewhere very close to this ion at a distance, say a, where a is the ion size parameter in this case and you are trying to get this small d Z i charge very close to this point. The amount of work that is done really in this case is nothing but the free energy change of the system.

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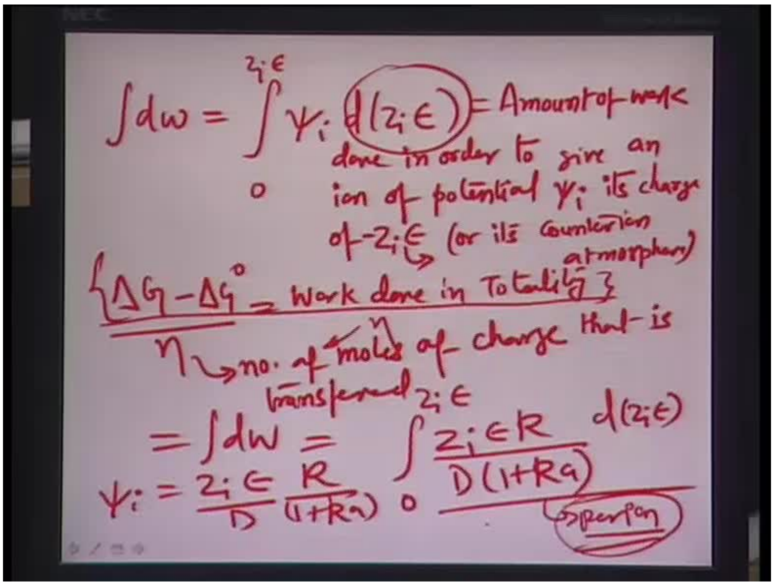

$\int dw = \int_0^{z_i\epsilon} \psi_i \, d(z_i\epsilon)$ = Amount of work done in order to give an ion of potential ψ_i its charge of $-z_i\epsilon$ (or its counterion atmosphere)

$$\frac{\left\{\Delta G - \Delta G^0 = \text{Work done in Totality}\right\}}{\eta}$$

$\eta \rightarrow$ no. of moles of charge that is transferred

$$= \int dW = \int_0^{z_i\epsilon} \frac{z_i\epsilon R}{D(1+Ra)} d(z_i\epsilon)$$

$\rightarrow$ per ion

$$\psi_i = \frac{z_i\epsilon}{D}\frac{R}{(1+Ra)}$$

The work that is stored in the system if allowed, the system can do an identical work. Let us find out what happens in terms of total work done. Let us assume this work is d w and we want to find out the total work done when all this charge, all this Z i E, is brought near to this point a, so, we can represent this by very simple integral d w and we assume that the d Z i varies from zero all the way up to Z i E, phi i times of d Z i E, that is what the total work done varies. This is actually nothing but equal to the amount of work done into the system done in order to give an ion of potential plus or phi i, its charge of minus Z i E or its counter ion atmosphere.

So, the delta G minus delta G naught for concentration equal to 1 is actually equal to the work done in totality per mole. This is the work done in totality. This divided by n, the number of moles of charge that is transferred can be equated to the integral d w. Therefore, we evaluate this integral 0 to Z i E times of phi i, and phi i is basically the counter ion contribution part of the potential; so, it is Z i epsilon k divided by D 1 plus k a times of d Z i E.

So far things are pretty clear that we are talking about trying to give an ion of potential psi i, its counter ionic charge of minus Z i E in bits and pieces of d Z i E. The total of amount of work done is computed by doing an integral as if the counter ion were zero before and it goes all the way to about Z i E. So, it is a kind of indirect way of looking at it. This is nothing but work done in totality by the number of moles because this is per ion. But delta G minus g is the work done in totality. So, you have to divide this on both sides by the number of moles of the charge that is transferred in order to equalize this work done per ion of interest. So, number of moles is essentially needed to make this work done per ion.

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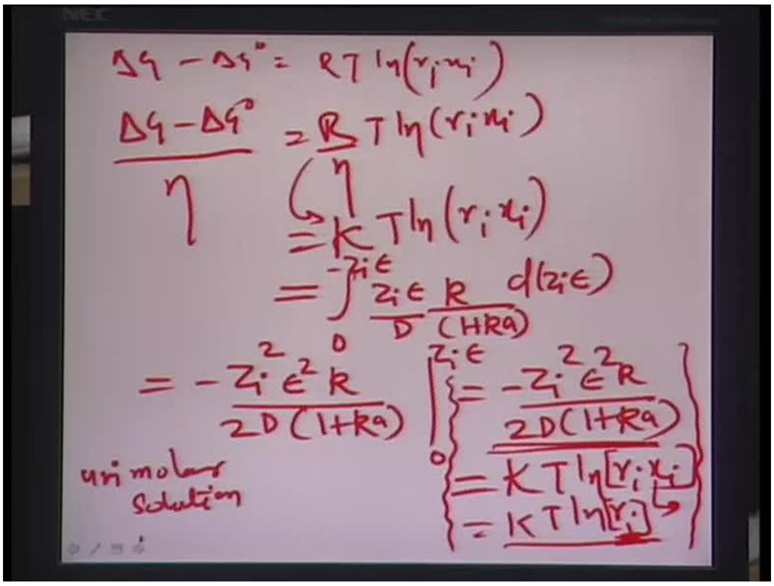

$$\Delta G - \Delta G^{0} = RT\ln(\gamma_i x_i)$$

$$\frac{\Delta G - \Delta G^{0}}{\eta} = \frac{R}{\eta} T\ln(\gamma_i x_i)$$

$$= KT\ln(\gamma_i x_i)$$

$$= \int_{0}^{-z_i \epsilon} \frac{z_i \epsilon}{D}\frac{\kappa}{(1+\kappa a)}\, d(z_i \epsilon)$$

$$= -\frac{z_i^2 \epsilon^2 \kappa}{2D(1+\kappa a)}\Bigg|_{0}^{z_i \epsilon} = -\frac{z_i^2 \epsilon^2 \kappa}{2D(1+\kappa a)}$$

$$= KT\ln[\gamma_i x_i]$$

$$= KT\ln[\gamma_i]$$

uni molar solution

If you look at the equation for delta G from before, delta G minus delta G 0 is equal to R times T l n of gamma i x i. Therefore, per ion, delta G minus delta G 0 by n should be equal to R by n T l n - l n of the activity gamma x i- l n of gamma i x i here. So, R by n is nothing but the Boltzmann's constant K. K is R by n, the Rid burg constant per mole of charge that is transferred times of K times of l n x i gamma i and this is equated to work done here which is essentially this factor zero0 to Z i E, and by the by this is the negative charge, minus Z i E Z i epsilon by D k times 1 plus k a times D Z i epsilon. If we do integral here, it will come out to be minus Z i square epsilon square k divided by twice D times of 1 plus k a varying between zero and Z i E, nothing but the same Z i E square times of epsilon square times of k divided by twice D 1 plus k a and this is equated to our earlier stance here, K T times of l n gamma i x i.

When we were talking about contribution per mole, the x i here can be considered to be for one mole. If we look at one mole of solution, this can be converted in to K T l n gamma i and therefore, for uni molar solution, the relationship between the total work done and the total free energy can be as given in these set of equations.

From this we have an important idea of what the activity in such an ion of interest would really be and therefore, let us in a little different manner try to see what gamma i is by taking antilog on both sides and trying to expand this term here on the left into a more appropriate and more readable term in terms of mean ionic strength of solution.

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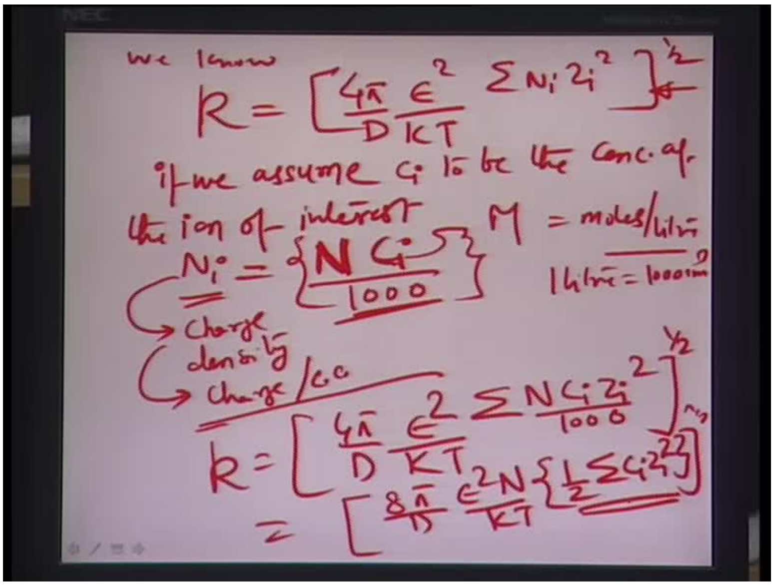

we know

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

if we assume C_i to be the conc. of the ion of interest

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

M = moles/litre

1 litre = 1000 cm³

charge density

charge/cc

$$K = \left[\frac{4\pi}{D}\frac{\epsilon^2}{KT}\sum \frac{N C_i z_i^2}{1000}\right]^{1/2}$$

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

We know that k is also 4 pi by D epsilon square by K T sigma N i Z i square to the power of half. We can do a little bit of change here with this N i term. If we assume that this C i to be the concentration of the ion of interest, the i th ion interest, then N i can be represented as the Avogadro number times of C i divided by 1000. N i, mind you, if you would have recalled from earlier, was the charge density, charge per unit volume. Since we were talking about CGS units, this is essentially charge per centimeter cube of volume.

C i of course is molarity, which is moles per liter and therefore, one liter is around 1000 centimeter cube and thus this 1000 term here. The number of moles or the number of charges per unit volume can be a function of N C i by 1000. So, if we substitute that back into this equation here, we can get the value of k as 4 pi by D epsilon square by K T sigma N C i Z i square divided by 1000 to the power of half. We can do further simplification and try to write this term in terms of 8 pi by D epsilon square N by K T times of half sigma C i Z i square whole half.

Now, this term is really a very interesting term and we can also call it the mean concentration in an ionic solution. All said and done, because we have utilized certain protocol or a certain way of notating the charge N i to be the negative charges and the positive charges and therefore, ultimately if suppose you have a CaCl 2 solution where you have a Ca plus 2 as the positive charge and Cl minus as the negative charge, the equation that you are finally going to derive out all of it can report about the activity should take into consideration because it is a different valency situations Ca has plus 2 and Cl has minus, but number of moles Ca is 1 Cl is 2.So, all these things have to be considered in the equation. That is why the notation that we had taken, N i was very important at the very outset.

Half C i Z i square here sigma is the mean concentration of all the different ions which are present. Suppose in a solution, if you have a CaCl 2, NaCl, KCl -these kind of competing ions over the ion selective electrode in question, in that case, half C i Z i square would be - suppose you have 1 mole of k c l present, so you have 1 concentration of potassium times Z i square which is 1 square plus 1 concentration of chlorine plus Z i which is minus 1 square. This is the way you had to keep on computing the mean concentration and divide the whole thing by 2, so that you have an idea what is the mean concentration of a solution.

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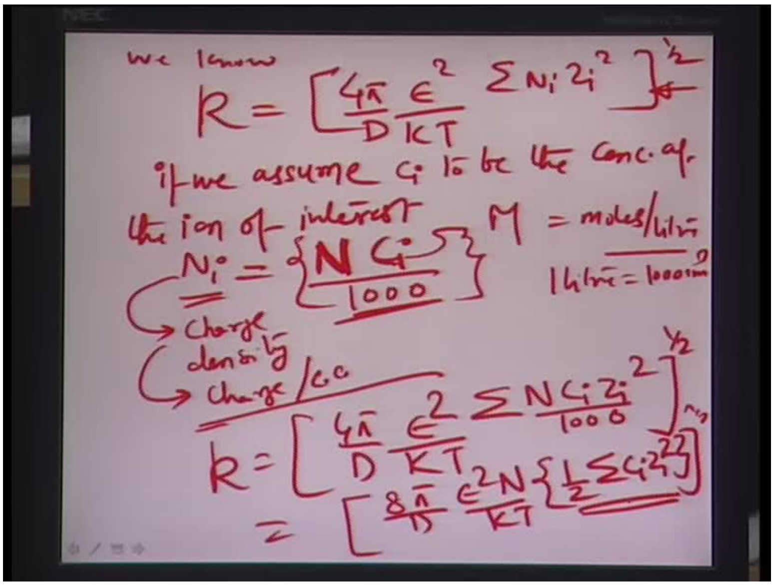

we know

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

if we assume C_i to be the conc. of the ion of interest

M = moles/litre

1 litre = 1000 ml

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

→ Charge density

→ charge/cc

$$R = \left[\frac{4\pi}{D}\frac{\epsilon^2}{KT}\sum \frac{N C_i Z_i^2}{1000}\right]^{1/2}$$

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

We are going to solve some examples later on where we will try to find out what this activity co-efficient would come in such a situation. From this equation here, we try to derive the final form of the equation for activity co-efficient in terms of the mean ionic strength which would be done in the subsequent lecture following this. Thank you!