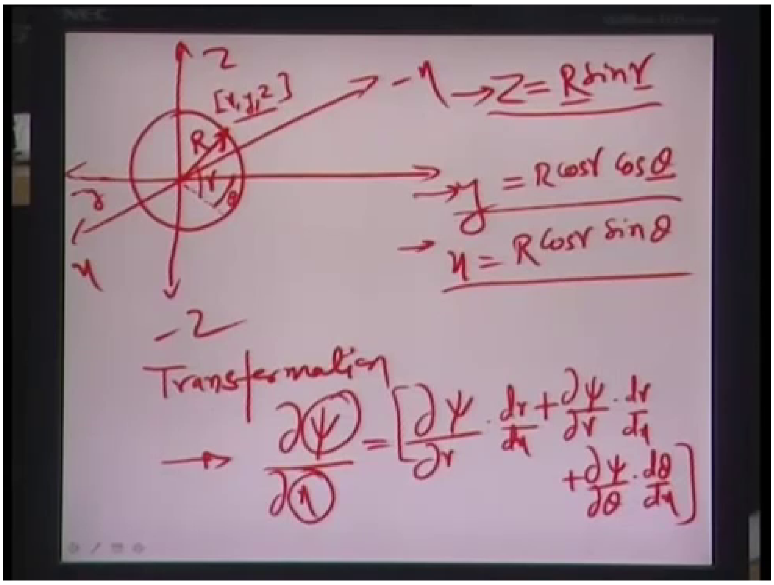
BioMEMS and Microfluidics
Prof. Dr. Shantanu Bhattacharya
Department of Mechanical Engineering
Indian Institute of Technology, Kanpur

Lecture – 08

(Refer Slide Time: 00:09)



$Z = R\sin\gamma$

$y = R\cos\gamma\cos\theta$

$x = R\cos\gamma\sin\theta$

Transformation

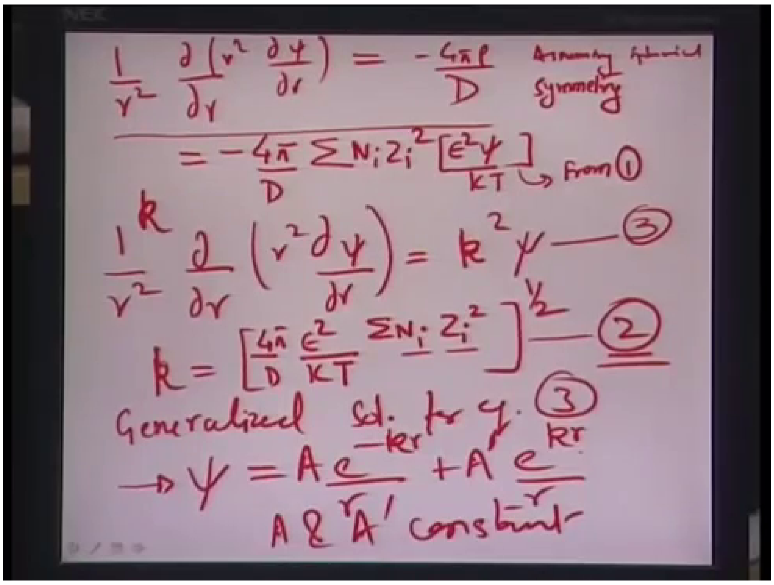
$$\frac{\partial\psi}{\partial x} = \left[\frac{\partial\psi}{\partial r}\cdot\frac{dr}{dx} + \frac{\partial\psi}{\partial\gamma}\cdot\frac{d\gamma}{dx} + \frac{\partial\psi}{\partial\theta}\cdot\frac{d\theta}{dx}\right]$$

So, welcome back to the lecture number 8 of this particular course. Last time we saw how to do the coordinate transformation and let me just take you through the same and before that we try to get in to this you know ionic activity and try to derive the activity coefficient using Debye-Huckle equation. So, we just about started on that after essentially completing the grand plot scheme of calibration and measurement of electrode. So, the coordinate transformation was needed, because we are trying to illustrate of you are trying to find out that mathematically the potential function. So, essentially you know use the Poisson's equation you know which is essentially space, special derivative of the potential function and equated that to in the charge density; you know $4\pi/\rho D$.

We also figure out that because we are talking about spherical central charge of interest and an ion cloud around that. We would have to deal with eventually with the spherically symmetric situation that will make our life easier and so therefore; we made a coordinate transformation of Cartesian to spherical. And this case we illustrated how we can find out this x y z, the point on the top of this radius vector with respect to R gamma and theta. Gamma being the angle between the projection of the radius in the x y plane and theta being the angle between one of the axis in this case the y axis; with this projection vector on the x y plane. And so essentially do the coordinate transformation and I would expect the students to actually go do and this is the part of the home work assignment I have been actually given.

So, if we consider the whole distribution and also consider you know spherical symmetry; that means, no variation what is ever with gamma or theta. So, spherical symmetry as if these potential functions are like shells around the small charge of interest, positive charge of interest.

(Refer Slide Time: 02:25)



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

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

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

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

Generalized sol. for ψ. ③

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

A & A' constant

In that case, the final equation falls down to $\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right)$. And this can be equated $\frac{-4\pi\rho}{D}$; alright. So, that is how the Poisson's equations can be written down, assuming spherical, spherical symmetric, assuming spherical symmetry. So, essentially the potential functions variation is purely with the respect to the radius vector r in that case. So, this can be further be kind of expanded in to by putting the value of rho that we obtained earlier in terms of you know, the subscript i and the total number of charges in the on the point A as $-\frac{4\pi}{D}\sum N_i Z_i^2\left[\frac{\epsilon^2\psi}{KT}\right]$; and essentially form 1. So, we have assumed this in equation number one in the earlier presentation.

So now, let us make some presumptions here, we just for the sake of convenience assume factor K, and this is actually you know this case different then the Boltzmann constant K. And actually let us in order to just make it a little more simplified and you know how without any problems. Let us consider this to be small k. So, written like this, small k. So, we can rewrite this equation as $\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right)=K^2\psi$.

There is what would be trying to look at, so let us just convert this into small k square phi. So, what is k square? Then in that case K is essentially a parameter which is equal to minus 4i or it is equal to 4 pi by D epsilons square by KT; where this case the Boltzmann constant, sigma Ni Zi square to the power half alright.

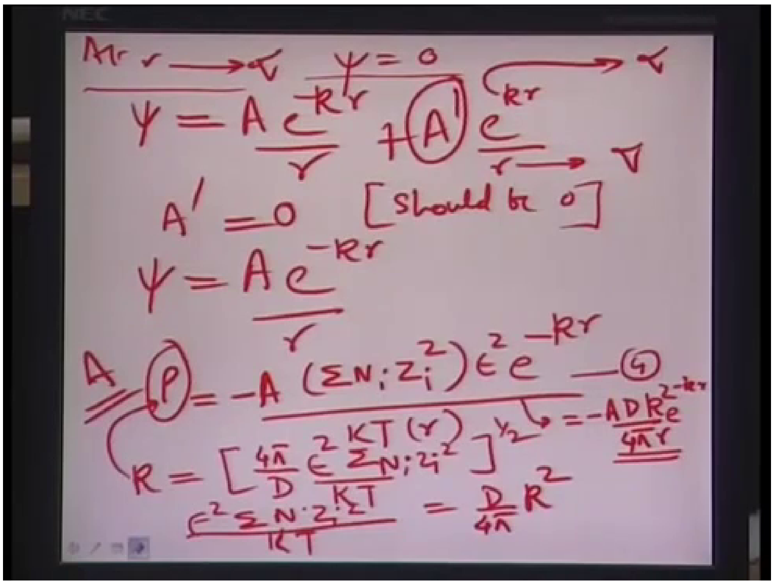
$$K=\left[\frac{-4\pi}{D}\frac{\epsilon^2}{KT}\sum N_i Z_i^2\right]^{1/2}$$

Let us actually write the such equation number two, is very important because very later on we have to you know write the final form final formulation in terms of the subscript i. And the various other parameter which are included in this, in this small k constant. Alright, let us call this equation three, alright.

So, if you go though you know p d is a partial difference equations again a you know any graduate program on them. There are generalized solution for representing a finding out this solution first, certain kind of p d is this case the generalize solution that one can think of equation three. So, generalized solutions for equation three comes out to be equal to phi equals $\psi=A\frac{e^{-Kr}}{r}+A'\frac{e^{Kr}}{r}$; alright. So, A and A dash are constants.

We should need to certain unknown, r of course is the radius vector and k as we know is given by equation two here. So, one way of checking back whether this is going to work or not is to put the value of pi in equation three; and see whether you have an equality in both sides ok. So, essentially if we put this root and try to evaluate the various aspects of the behavior of potential function; that means, what we know as boundary conditions of the potential function would be able to estimate this coefficient A and a dash. Let us look at it how.

(Refer Slide Time: 07:20)



At r → ∞ ψ = 0

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

A' = 0 [Should be 0]

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

$$\rho = -A\frac{(\Sigma N_i z_i^2)\epsilon^2 e^{-Kr}}{KT(r)} = -\frac{ADK^2 e^{-Kr}}{4\pi r} \quad (4)$$

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

$$\frac{\epsilon^2 \Sigma N_i z_i^2}{KT} = \frac{D}{4\pi}K^2$$

So, as we know there at r equal to infinity, at r tends into infinity the potential function phi be also equal to 0. That is what the basic premise was when we are talking about central charge distribution and you know, ion cloud that the potential generating from this small ion of interest; positive ion of interest at distance which is the infinitely spaced you know would be 0 essentially. There is no potential at infinity. So, therefore, if you assume phi to be 0 at r equal to infinity, and if we know from earlier that the equation for phi is $\psi = A\frac{e^{-Kr}}{r} + A'\frac{e^{Kr}}{r}$. Then the only way you can have this condition r equal to infinity, $\psi = 0$ validate is by assuming the A' is equal to 0, should be equal to 0. For obvious reasons right, because if r is essentially, if r is give me minute here.

So, if r is infinity then in that case this particular term here e^{Kr} should also go to infinity right and r being infinity. The only way to avoid the situation is by assuming 0 coefficient. So, that you know there is validation. So, therefore, really phi is represented as e^{-Kr}, minus k r excuse me. By r and as we know from earlier that the rho essentially the charge density is also minus A times of sigma N i Z i square epsilons square e to the power of minus k r by K T times of r. So, essentially this is same as writing minus you know sigma Ni Zi square phi by KT. Phi being e to the power of A e to the power of minus k r by r. So, we have just made a slight to rearrangement here for the charge density.

$$\rho = \frac{-A\left(\sum N_i Z_i^2\right)\epsilon^2 e^{-kr}}{KT(r)}$$

So, in other words you know this essentially this value. So, you know if we look at the equation number two earlier, that we have done before this in terms of k how we can represent this whole expression. So, then from there we can easily get that k here, if you look at has been represented as 4 pi by D epsilons square phi I am sorry, not phi; phi is actually outside. So, K square epsilon square 4 pi by d Boltzmann constant K times of T sigma Ni Zi square to the power of half, alright.

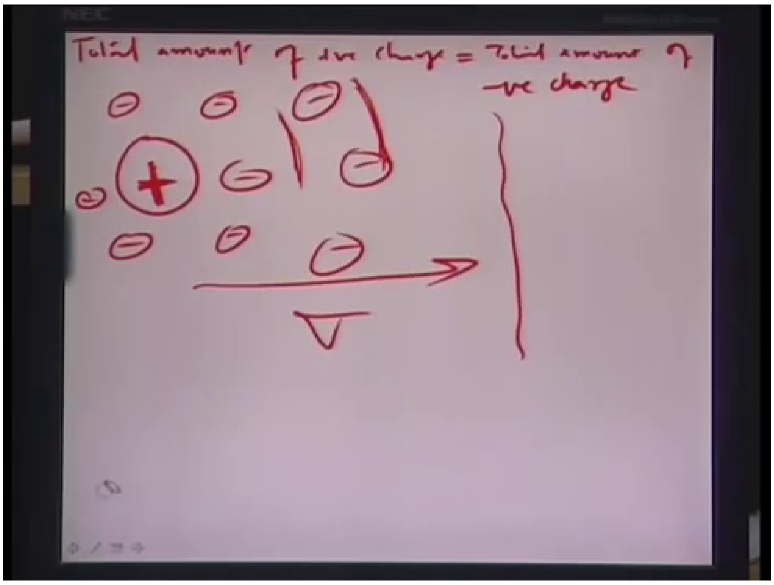
$$K = \left[\frac{4\pi}{D}\frac{\epsilon^2}{KT}\sum N_i Z_i^2\right]^{1/2}$$

And so, we can do a little bit of manipulation here. So, that we can represent this whole term in terms of k, and so essentially from here we can also have an expression where in the essentially the epsilons square sigma Ni Zi square by KT term dues to, just give me I mean clear.

So, epsilon square sigma Ni Zi square by K T term. The k here, this k is Boltzmann constant kind of represented as D by 4 pi small k square right. $\frac{\epsilon^2}{KT}\sum N_i Z_i^2 = \frac{D}{4\pi}R^2$ And so, if i substitute that back in to this equation four here, the final equation that are I get 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 denominated, alright.

So, basically A k square D and sense this particular term as you know it, this can be you know represented as $\frac{-ADK^2e^{-kr}}{4\pi r}$. So, this is an important aspect, because this is essentially what the charge density at point A; really yes. Now we will like to have a look at what is really the corresponding counter ion clouds charge density. So, for doing that as we are wear that the principle of electron neutrality is always to be followed.

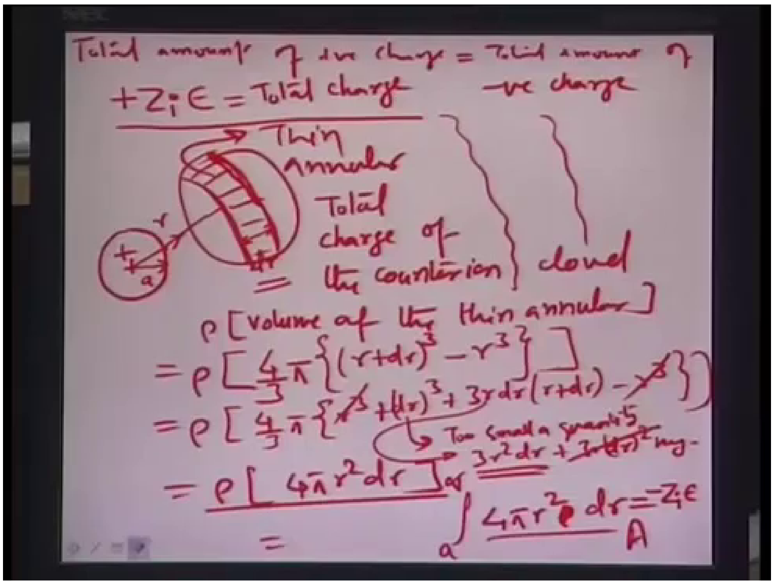
(Refer Slide Time: 13:27)



Total amount of +ve charge = Total amount of -ve charge

So far 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 a 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, right exactly. So, essentially the total charge in the ionic atmosphere, let say all the way up to infinite here it is going to infinity. So, there are charges here, there are charges here. So, there is essentially a whole bunch of this counter ion charges assuming a single positive charge all the way up to infinity. We should totally be able to balance in this particular charge. If we assume that and if we try to find out, what is really this charge density of the counter ion cloud? And equate that two just the negative magnitude of the positive charge here, we should be able to get a quality between the two, alright. So, let us try and do that and then with the charge density that, we have figured out in our earlier slide. Will try to find out what the coefficient A really would be. And this is a women's utility for us as we will see later because a essentially you know all this ionic activity and ion selective electrodes, do depend a lot on how this particular behavior you know of surrounding ions would be effecting the electrical contribution of the particular ion of interest in this case, in our case it is the positive ion; alright.

(Refer Slide Time: 14:55)



Total amount of +ve charge = Total amount of

$+Z_i \epsilon$ = Total charge   −ve charge

Thin Annular

Total charge of the counterion } cloud

$= \rho$ [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

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

$= \rho\left[4\pi r^2 dr\right]$ or

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

A

So, let us assume the central charge to have you know plus Zi epsilon as the total charge. So of course, if I have let say positive ion here and this has let say some kind of radius where let us assume that if you have a you know, some distance actually at A which is very close by here the radius A. And we assume that this, there is an ion cloud which extends all the way up to infinity let say, but then at this distance r from this center at distance r from the center, we are trying to see what is the charge density in a thin shell of the counter ion clouds. Let us assume that this is thickness of this shell is as small as an infinite is similarly small value of the radius function r here as dr. So, the total charge that way if want to find out. So, the total charge of the counter ion cloud would be represented as with the charge density times the volume of this thin annular. Assuming this is a thin annular, spherical annular. So, we need to find out what is the total charge stored in this spherical annular, by looking at this volume here. So, we get this as rho times of let us assume that you know, you have essentially thin ring which you can open and closed and which has total let say.

So, basically of the volume of the thin annular here is we are talking about this essentially you know $\left[\frac{4}{3}\pi\{(r+dr)^3 - r^3\}\right]$, right. We assume that to we are trying to calculate the volume of this thin annular here. So, the radius vector all the way have to here is the r plus dr and here it is r. So, essentially we are trying to create a volume difference. So, let us actually try to look at what this volume would be like. So, essentially a 4 by 3 pi and then we have r cube plus d r cube plus 3 r dr times plus r plus dr minus r cube, alright.

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

$$\rho\left[4\pi r^2 dr\right]$$

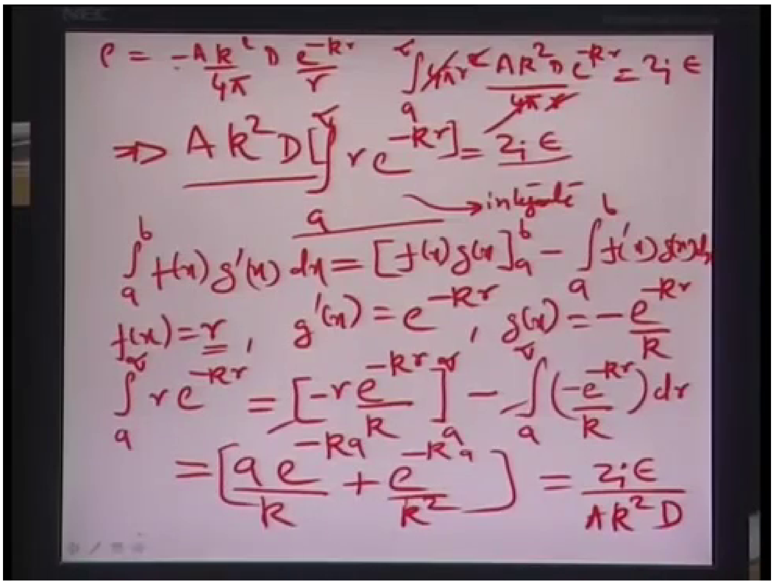
This can canceled away, this is two small a quantity and. So, essentially if we look at this quantity here, it is 3 r square d r plus 3 r dr square. We assume d r to be so small that even this is neglected. So, we are left with only $4\pi r^2 dr$ as the elemental volume here in this particular annular. And so therefore, if we want to calculate the total charge you know, in this thin annular it would be and total charge of the counter ion cloud.

So, we can actually give a boundary condition here, the as if the density has to be calculated from the radius of the basic ion A all the way to infinity of this expression $4\pi r^2 \rho dr$. And this essentially is nothing but, an integration of the of the surrounding ions ion density or ionic concentration. And what this should be equal to really, as i told before that you know for the principle of electro neutrality this should be equal to you know the negative of the charge as the primary as the charge of the primary ion of interest, which is the positive charge.

$$\int_a^\infty 4\pi r^2 \rho dr = -Z_i \epsilon$$

So, essentially from this equation we should be able to get some information about the parameter A as we had actually define before while calculating, the density rho. Let us look at how we do that; alright.

(Refer Slide Time: 20:31)



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

$$\Rightarrow \underline{A k^2 D} \left[\int_a^{\infty} r e^{-kr}\right] = Z_i \epsilon \longrightarrow \text{integrate}$$

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

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

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

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

$$f(x) = r$$

$$g'(x) = e^{-kr}$$

$$g(x) = \frac{e^{-kr}}{k}$$

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

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

So, essentially rho again from the earlier equation at come out to be minus A K square by 4 pi give me a minute. So, this k here is the small k, should not confuse between both the both the different case. So, minus A k square by 4 pi times of D dielectric constant times of e to the power of minus k r by r.

$$\rho = \frac{-A k^2}{4\pi} D \frac{e^{-kr}}{r}$$

Ok that is what rho is, and 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, alright. That is what, this particular k is really k r.

$$-\int_a^{\infty} 4\pi r^2 \times \frac{Ak^2}{4\pi} D \frac{e^{-kr}}{r} dr = -Z_i \epsilon$$

So, in a nut shell this is equated to Zi times of epsilon for you know being electrically neutral in the case of electro neutrality; mind you that this is because this being negative sign. The negative sign on the right cancels because of the. So, let us actually try to integrate does not find out what comes.

So, this 4 pi by goes away, that is first power in the 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.

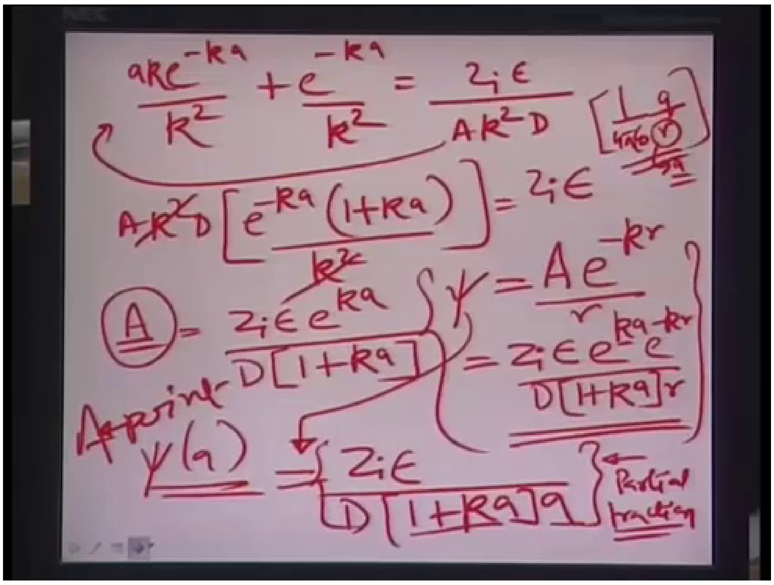
$$Ak^2 D \left[\int_a^{\infty} r e^{-kr} dr \right] = -Z_i \epsilon$$

So, we will like to integral this by part, alright; and you know this. So, essentially we integrate them by parts we know that you know between a and b, f x g dash x dx; 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 retreat what integral by parts. $\int_a^b f(x) g'(x) dx = [f(x) g(x)]_a^b - \int_a^b f'(x) g(x) dx$

So, essentially here f x equal to a, the f x here essentially equal to r; and g x here is equal to e to the power of minus k r. So, naturally this g dash is equal to e to the power of minus k r. So therefore, g x becomes minus e to the power of minus k r by k, alright. So, that is what g x becomes. So therefore, and we are trying to calculate integral a to infinity r e to the power of minus k r, we are essentially doing minus you know r e to the power of minus k r by k. The 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 one because of x is r dashes nothing but d by d r of a function r times of g x, which is minus e to the power of minus k r by k, d r. So, that is what this integral would be eventually looking like and solving this equations, on solving this equation we kept, so final value here as a e to the power of minus k a by k plus e to the power of minus k; give me minute, e to the power of minus k a by the k square. That is what the final integral would look like after we put the value of r between a and infinity and evaluate this term one and term two here, in this particular equation. So, that is what essentially the Zi E would really be, Z i E really be.

So, starting from here should get an idea of what a would be; because a is a essentially in the potential term and from the differential equation a is essentially also unknown so far and we need to estimate the value of capital A. So, essentially this would be only method of doing that. Let us look at by solving what the value would come out to be equal to. So, we just rewrite this particular, if you look back here the value of I am sorry. Look back here the value of the A k square D in to the integral which we had just try to find out this Z i E right. So, the this becomes Z i E by A k square D. So, we take this equation the next page.

(Refer Slide Time: 26:42)



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

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

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

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

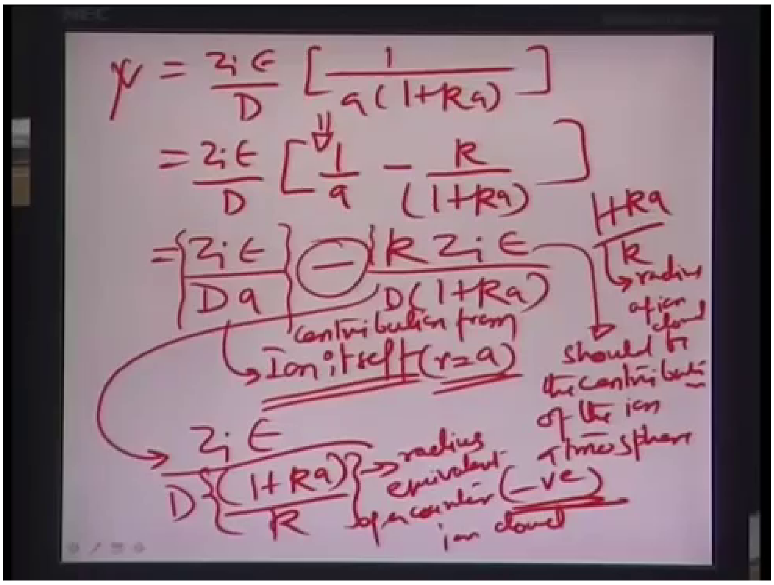
$$\psi(a) = \frac{Z_i \epsilon}{D[1+ka]a}$$

So, 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 essentially to Zi E by a k square D; right. So, let us take this term here sight, so 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, z i times epsilon. And 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; right. So, that is what the value of A is, the coefficient 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. So, 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 of divided by D 1 plus k a, small a times of r. So, that is what the potential function phi and that particular point is. So now, we have pretty much every thing known, we know what k is, we still do not know what a is and this a essentially is also known as the ion size parameter as we look at in the next slide, alright.

So, at the first thing which comes to our mind is let us really find out what psi at a is. That essentially what the potential function at the point A really was. So, if i put the value of a in this particular equation here alright, 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 equal to a the cancel out; alright. So, let with Z i epsilon by D times of 1 plus k a times of a. So, this is gives as an interesting observation. We can try to kind of independently make these two coefficients on two different terms in the denominator or we can try to solve this particular equation using partial fraction concept to interpret about what is the contribution of the ion and the potential ion what is the contribution of the surrounding ion atmosphere right. Because potential as you know, is nothing, but 1 by 4 pi epsilon not, some charge contribution let say q divided by the radius of the distance of a point from that particular charge. In this case the distance that we are considering is a right, so let us actually aspect is using partial fractions.

(Refer Slide Time: 30:37)



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

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

$$\frac{Z_i \epsilon}{Da} - \frac{kZ_i \epsilon}{D(1+ka)}$$

So, if you try to do that in the phi value can be which is represented as let me just borrow what I did in the last slide for convenience; and so 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. The just compute this if you make this you know the denominator will come out to be a times of 1 plus k a. And one plus k will be here minus k times of a. So, that essentially this is 1 by a into 1 plus k a. So, this is the correct partial fraction for this special on the top. And let us equated two different terms Z i by D times of a minus k divided by D times of 1 plus k a. So, times of Z i E. So, what we are share about one thing is that you know, this probably corresponds to the contribution from the ion itself; from the ion itself as corresponds to an r value equal to a as we had investigated before.

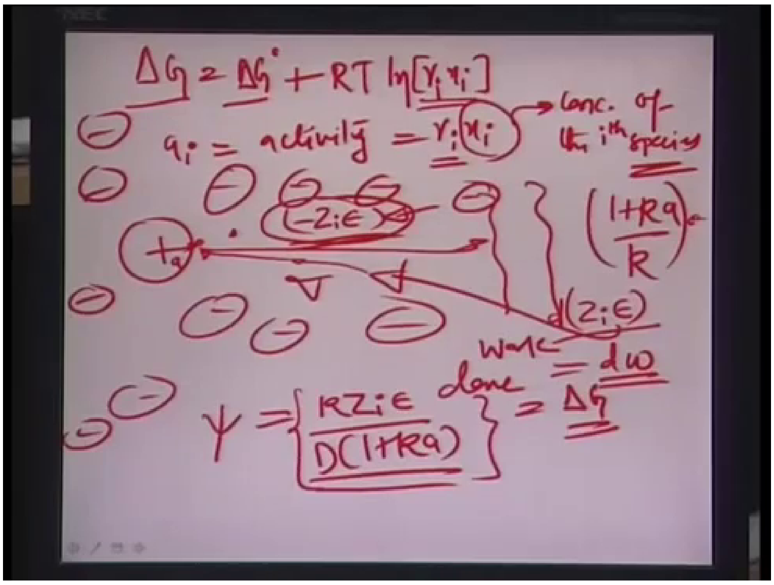
Radius value equal to a and this should be because even it is negative, as you can see here should be the contribution of the ion atmosphere.

So, this is a very important fact you know, that this is a negative ion atmosphere as we know right; because a central ion was positive. And so therefore, the contribution to the potential function by this particular term here is also negative. So, the 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 with surrounding it. So therefore, if we kind of try to estimate what is an average radius or what is an equivalent radius of such counter ion cloud, I could write this down very well as Z i E by D times of 1plus k a by k. So, this is a kind of radius equivalent of a counter ion cloud. So, this is a radius equivalent of a counter ion cloud and which might mean that 1 by k, 1 plus K a i am sorry. Let me just write this term again, 1 plus k a by k is the radius of ion cloud.

So now, let us go to another very important aspect that, how we can correlate this to all these information really to the activity of the particular ion of interest which is positive and this case. So, so basically we would now like to find out how all whatever we have done so for is a related to the activity of ion of interest. And for that there has to be some kind of relationship in terms of the amount of work that is done you know, for bringing a small amount of let say the counter ion cloud from infinity into the center of the counter ion cloud; and try to equate that to delta G equation, the free energy, the Gibbs free energy equation. And by this will be clear in a little bit when I just demonstrate that part. So, let us see, let us study first, that what really would be the free energy involved in a all these process where the ions kind of you know come from infinity and you know the form a counter ion of minus Z i E. We around the surround you know around the main ion of interest which is plus Z i E. So, how all that happens and you know that the work done the amount of maximum work done which is also equal to the free energy of the system how that can be define in terms of ionic concentration.

So, as we know from before from the van't hoff equation, while doing electrochemical cells we found out that the amount of free energy of such a cell for nice in system would be delta G, would be given by the equation delta G equal to delta G not plus r times t natural log off activity of the ion which is gamma i x i, right.

(Refer Slide Time: 36:06)



If you remember when we talked about the activity ionic activity and in fact, when we were discussing the electrochemical cell we consider that, there is a lot of high ionic background and therefore, there is only one specific ion of interest and. So, the activity question gamma is 1 in that case. But in our case here really the activity coefficients. So, that is why the activity was a function of concentration here though the activity is because of the several interacting ions that represent in the solution, a finite you know value gamma i into the concentration of the i-th species. So, we do get relationship between the free energy associated with this dynamics that is going on round the positive ion and the activity of the particular species of interest.

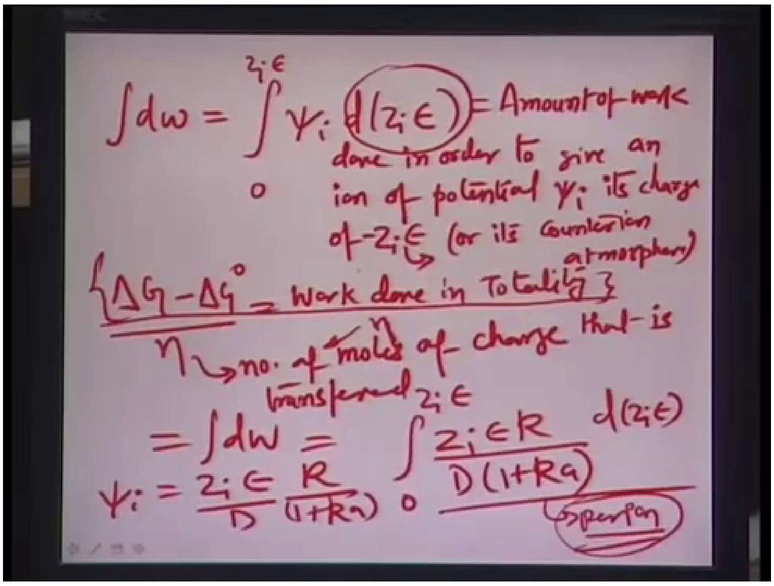
$$\Delta G=\Delta G^0+RT\ln\left[r_i x_i\right]$$

So, let us see what would be needed, to bring let say a few moles of the counter ion cloud from infinity into such a cloud. So, let say you have a positive ion here, this is the infinite playing probably. And there is a bunch of counter ion clouds which are surrounding in 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. So now, also then done let say this kind of charge distribution is existing and you want to bring some charge, some elementary charge let say and let us also assume that this is minus Z i Epsilon. We assume that this total counter ionic charge is minus Z i Epsilon. You make this presumption while deriving this ionic radius formulation of the cloud.

So, we assume that a very small amount of this charge let say 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. Maybe at a put at a point where the potential is also defined by the formulation you know K Z i, 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, from the negative. And so if you have a potential function somewhere very close to this ion, you know at distance say a where is the ion size parameter in his 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. And the work that is stored in the system; if allowed the system can do an identical work. So, let us find out what happens in terms of total work done. Let assume this work is d w and we want to find out the total work done; when all these charge, all this Zi E is brought near to this point a.

$$\psi = \frac{kZ_i\epsilon}{D(1+ka)}$$

(Refer Slide Time: 40:06)



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

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

n → no. of moles of charge that is transferred

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

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

[illegible]

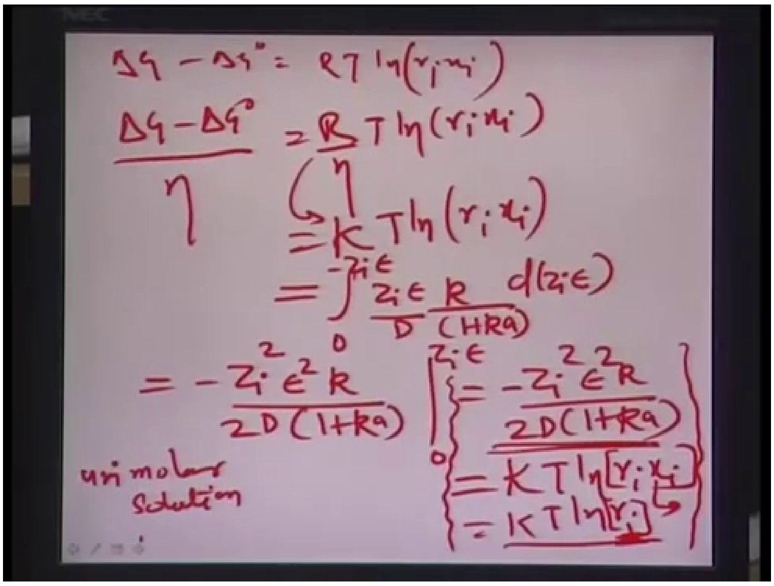
$$\int dw = \int_0^{Z_i\epsilon} \psi_i d(Z_i\epsilon)$$

$$\Delta G - \Delta G^0 = \int dw = \int_0^{Z_i\epsilon} \frac{kZ_i\epsilon}{D(1+ka)} d(Z_i\epsilon)$$

So, we can represent this by just you know, very simple integral d w and we assume that the d Zi varies from 0 all the way up to Zi E phi i times of d Zi E; that is what the total work done varies. So, this is actually nothing but, equal to the amount of work done into the system, done in order to, in order to give and ion of potential plus or phi i its change its charge of minus Zi E or its counter ion atmosphere. So, the delta G minus delta G naught for concentration equal to 1, which is actually equal to the work done in totality right, work done in totality per mole. So, essentially this is for this is the work done is totality. So, this divided by n the number of moles of charge, that is transferred can be equated to the integral dw, right. So, therefore, you know we evaluate this integral 0 to Zi E times of phi i and phi i you know from earlier thought is basically in the counter ion contribution part of the potential. So, its Zi Epsilon k divided by D 1 plus k a time of d Zi E.

So, for things are pretty clear that you know we are talking here about trying to give an ion of potential phi i, its counter ionic charge of minus Zi E. In bits and pieces of d Zi E and then the total amount of work done is computed by doing an integral, as if the counter ion 0 before and it goes all the way to about Zi E. So, it is a kind of indirect way of looking added. So, this essentially is nothing but, this work done into totality by few number of moles, because this essentially is again per; ion this is per ion alright. So, but delta G minus G essentially is the work done into totality, alright. So, you have to divide this on both sides by the number of moles of the charge that is transfer 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.

(Refer Slide Time: 44:37)



$$\Delta G - \Delta G^{\circ} = RT\ln(r_i x_i)$$

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

$$= kT\ln(r_i x_i)$$

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

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

$$\Big|_0^{z_i\epsilon} = -\frac{z_i^2\epsilon^2\kappa}{2D(1+\kappa a)}$$

$$= kT\ln[r_i x_i]$$

$$= kT\ln[r_i]$$

unimolar solution

$$\Delta G-\Delta G^0=RT\ln\left(r_i x_i\right)$$

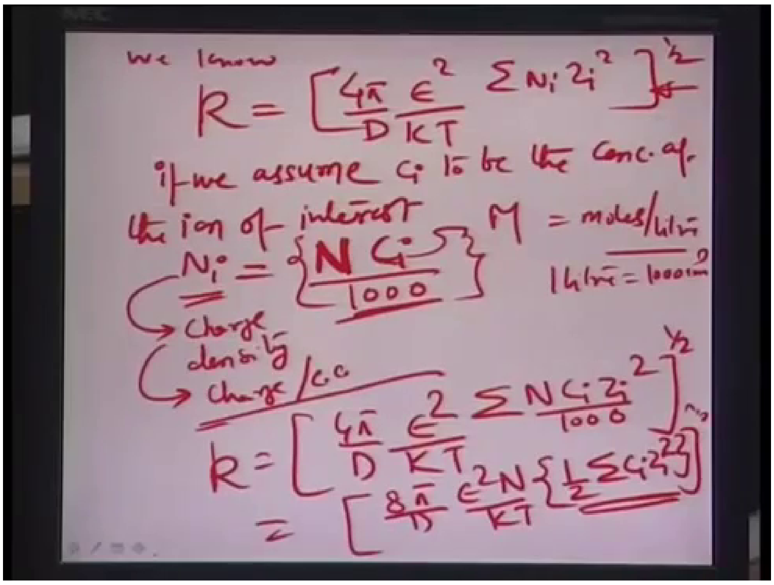
$$\frac{\Delta G-\Delta G^0}{\eta}=\frac{RT\ln\left(r_i x_i\right)}{\eta}=KT\ln\left(r_i x_i\right)$$

$$\int_0^{Z_i\epsilon}\frac{kZ_i\epsilon}{D\left(1+ka\right)}d\left(Z_i\epsilon\right)=\left[\frac{kZ_i^2\epsilon^2}{2D\left(1+ka\right)}\right]_0^{Z_i\epsilon}$$

So, if you look at the equation for delta G from before $\Delta G-\Delta G^0=RT\ln\left(r_i x_i\right)$. And so therefore, you know per ion $\frac{\Delta G-\Delta G^0}{\eta}=\frac{RT\ln\left(r_i x_i\right)}{\eta}=KT\ln\left(r_i x_i\right)$. So, R by n as we know is nothing but the Boltzmann constant K. K is R by n the red box constant for whole of charge that is transfer times of K times of l n x i gamma i; and this is equated to our work done here which is essentially this is factor 0 to Zi E. And by the by this is the negative charge so, it is minus Zi E, Zi epsilon by D k times 1 plus k a times d Zi epsilon. And essentially if you did integral here, it will come out to be minus Zi square epsilon square k divided by twice D times of 1 plus k a varying between 0 and Z i E. So, essentially nothing but the same Z i E square, is a Zi, Zi square times of epsilons square times of k divided by twice D 1 plus k a. And this is equated to our earlier stands here KT times of l n gamma i x i, alright.

So, when we are talking about contribution per mole, the x i here can be consider to be for 1 mole. So, at essentially if you look at 1 molar solutions, 1 molar solution this can get converted into KT ln gamma i right; and so therefore, for uni molar solution the relationship between in the total work done and the total free energy can be as given in the set of equations. So, from this though 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 manor try to see what gamma i is taking by antilog on both sides and trying to expand this term here on the left to into a more appropriate or more readable term in terms of mean ionic strength of the solution.

(Refer Slide Time: 47:58)



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

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

M = moles/litre

1 litre = 1000 cm^3

→ Charge density

→ charge/c.c

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

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

$$k=\left[\frac{4\pi}{D}\frac{\epsilon^2}{kT}\sum N_i Z_i^2\right]^{0.5}$$

So, here 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, right. So, the we can we can do a little bit of change here with this N i term, that if we assume that you know this C i to be in the concentration of the ion of interest. The i-th ion of interest. Then N i can be represented as the number of moles N C i times of; so that means, the number of, there is the Avogadro number. This is the Avogadro number; times of C i divided by 1000. Can I remind you if you would have a recall from earlier, was the charge density. So, charge per unit volume and since you are talking about CGS units. So, this is essentially charge per 1000 c c or per c c I am sorry. Charge per centimeter cube of volume, charge per centimeter cube of volume. So, C i of course, is a molarity which is moles per liter and therefore, 1 liter is round 1000 centimeter cube and thus this 1000 term here. So, essentially the number of moles or the number of charges per net volume can be a function of N C i by 1000. $N_i=\frac{N C_i}{1000}$ So, if you 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 Ci Zi square divided by 1000 to the power of half. And essentially we can take, we can do for the simplification and try to write this terms, in terms of 8 pi by D epsilon square N by KT times of half sigma Ci Zi square whole half. Now this term is really very interesting term and we can also call a the mean concentration, or you can call it the mean concentration in ionic solution. Now all sudden done because we have utilized certain protocol or a certain way of notating the charge N i to be the charges, the negative charges on the positive charges. And so therefore, you know ultimately if suppose you have a CaCl2 solution where you have a Ca plus 2 as the positive charge and C l minus as the negative charge.

The equation that you are finally going to derive out of all it, all of it where it can report about the activity should take into consideration, because it is a different valance situation; a has plus 2, C l has minus. But number of moles C a is 1, C l is 2. So, all these things have to be considered in the equation, that is why the notation that we have taken N i was very very important at the vary outside. So, half C i Z i square here sigma is essentially a mean concentration of all the different ions which are present. Now suppose in a solution if you have Cs Cl to, NaCl, KCl these kind of computing ions over the ion selective electrode in question. So, in that case half Ci Zi square would be suppose you have 1 mole of KCl represent. So, you have 1 concentration of potassium times Zi square which is 1 square, plus 1 concentration of chlorine plus Zi which is minus 1 square. So, this is the way you have to keep on computing the mean concentration divide the whole thing by 2. So, that you have an idea what is the mean concentration of a solution.

$$k=\left[\frac{4\pi}{D}\frac{\epsilon^2}{kT}\sum\frac{NC_i}{1000}Z_i^2\right]^{0.5}=\left[\frac{8\pi}{D}\frac{\epsilon^2 N}{kT}\frac{1}{2}\sum C_i Z_i^2\right]^{0.5}$$

So, we are going to also solve some examples later on, where will try to find out what this activity coefficient would come in such a situation. So, from this equation here we try to derive the final form of the equation for activity coefficient, will terms of the mean ionic strength which would be done in the subsequent lecture following this.

Thank you.