BioMEMS and Microfluidics
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Lecture – 07

To do a just quick review of what was covered in the last lecture before trying to you know beginning this a new lecture.

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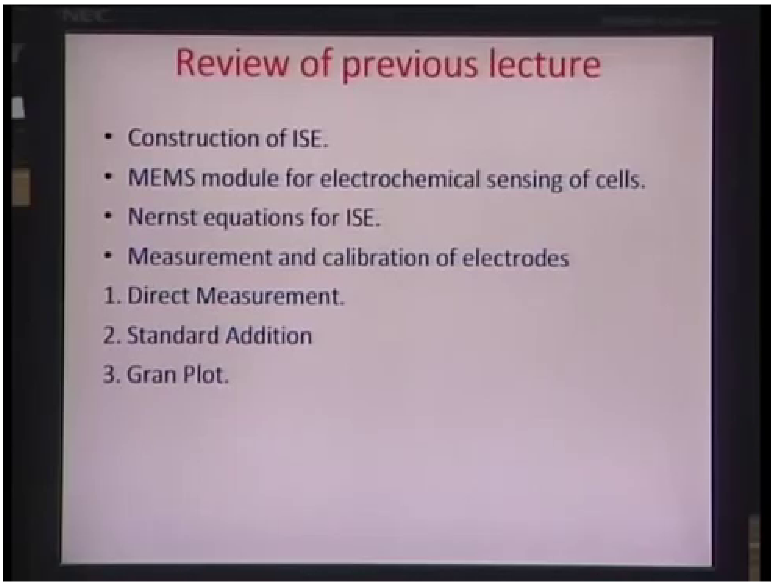

Review of previous lecture

- Construction of ISE.
- MEMS module for electrochemical sensing of cells.
- Nernst equations for ISE.
- Measurement and calibration of electrodes

1. Direct Measurement.
2. Standard Addition
3. Gran Plot.

So, the last session we discussed at length about the construction of ion selectivity electrodes. Ion selective electron essentially are those electrodes which has a tendency of selecting 1 or more ions of interest over a bunch of different ions. And there are certain motility which we need to consider before you know explore the how to construct these typically, you have to have kind of recognition agent by identified select which can offer selectivity. So, one way of doing it as we learnt last time is basically preparing polymer pace like polymerized chloride and then, trying to new include next material which is causing the selectivity or the selection action. One fantastic example was that the valinomycin were these essentially organic extracts available on the cell membrane and which can help to basically exchange calcium and potassium ions. So, if you want to make a calcium selective or potassium selective electrodes you have to have this valinomycin in this polymeric material.

The way you prepare electrode is that you take the sin glass capillary, you deep it and create a plug kind of a thing which is also like a ion exchange membrane and then, basically fill that with certain electrolyte immerse a conduit which can do the electrical measurement from that electrolyte. We also talked at length about the various ways, alternative ways and means of making the ion selective electrodes. One of them if you remember was with 2 different oxidant concentrations and that avoided the need for reference electrolyte as has been the case in all the ISC's.

We talked and discussed about MEMS modules for electrochemical sensing of cells wherein we showed small silicon chip and showed 64 according channels where there could be single cell by single isolation and the electrodes could recorded response from to cells etc. Then, we tried to derive the famous Nernst equation, which is also equation meant for describing relationship between the emf and the log of concentration. We found out that, you know the Nernst slope is a equivalent to parameter s which is essentially 0.059 by n and being the number of electrons which are exchanged in the redox couple. We also tried to estimate the emf in some numerical problems, if the concentration of a certain analyte is known or vice versa. And then, we talked essentially about how to measure and calibrate such electrodes and we discussed about 2 different techniques; direct measurement, wherein you just find out the emf for certain concentration using the Nernst approach.

Standard addition method you will use the standard concentration and a standard volume and then, find out the new concentrations and from the 2 emf that you get could actually gage, you know what is the unknown concentration. If the standard concentration in the volume of the unknown solution and volumes and standard solution they are all known. We were just about begin to talk about Gran plot and what I am going to do today is to take you off from here and go through the Gran plot, just once more for the sake of viewing and then do numerical problem and move ahead. So, the third method which we slightly discussed the last day was the Gran plot.

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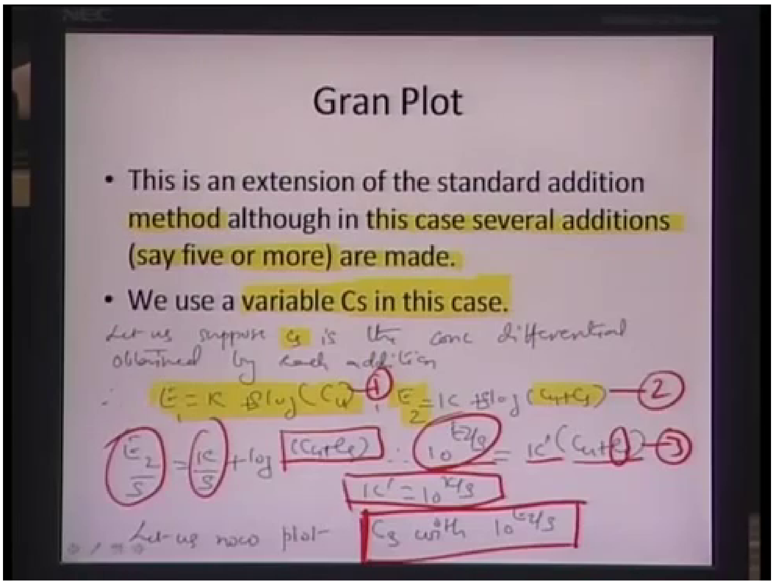

Gran Plot

- This is an extension of the standard addition method although in this case several additions (say five or more) are made.
- We use a variable Cs in this case.

Let us suppose C_s is the conc differential obtained by each addition

$\therefore E_1 = K + S\log(C_u)$ — ① , $E_2 = K + S\log(C_u + C_s)$ — ②

$\frac{E_2}{S} = \frac{K}{S} + \log \boxed{(C_u + C_s)}$ $\therefore 10^{E_2/S} = K'(C_u + C_s)$ — ③

$\boxed{K' = 10^{K/S}}$

Let us now plot $\boxed{C_s \text{ with } 10^{E_2/S}}$

You know this is essentially an extension of the standard addition method, all though in this case several additions say 5 or more are made. So, in this particular method there is you know several additions of a known concentration analyte. So, here we define Cs as a variable in manner that this Cs essentially is a concentration where you know, this is basically the concentration differential. So, if you are adding a certain concentration to the unknown concentration of the analyte and the overall concentration that comes out because of this addition of known volumes of the standard, know volumes of the unknown that can have or can be represented as the unknown plus differential, a concentration differential. So, that differential is Cs.

So, we are just redefining you know the parameters Cs slightly in a different manner. And this should be very clear at the outset because sometimes there is a confusion because of that in solving numerical solving. So, let us suppose that, Cs is such a concentration and if you talk about a known light of concentration Cu, you can find out the emf from this particular equation $E_1 = K + S\log(C_u)$. This is the Nernst approach to determine the emf and let us suppose after the addition, the new concentration becomes Cu plus Cs; Cs being the differential concentration and the new emf E 2 can be written down as $E_2 = K + S\log(C_u + C_s)$. So, if this is treated as equation 2 here you know. Let us supposed this is equation 1, this is equation 2.

The equation 2 can be again redefined as $\frac{E_2}{S}=\frac{k}{S}+\log\left(C_u+C_s\right)$. And therefore, $10^{\frac{E_2}{S}}=k'\left(C_u+C_s\right)$. And K dash essentially here is $k'=10^{\frac{k}{S}}$. Let us now plot Cs with E to the power of $10^{\frac{E_2}{S}}$. So, essentially this equation here, equation 3 you just like straight line. So, between Cs and 10 to the power of E 2 by S, the relationship is something like y is equal to m x plus c.

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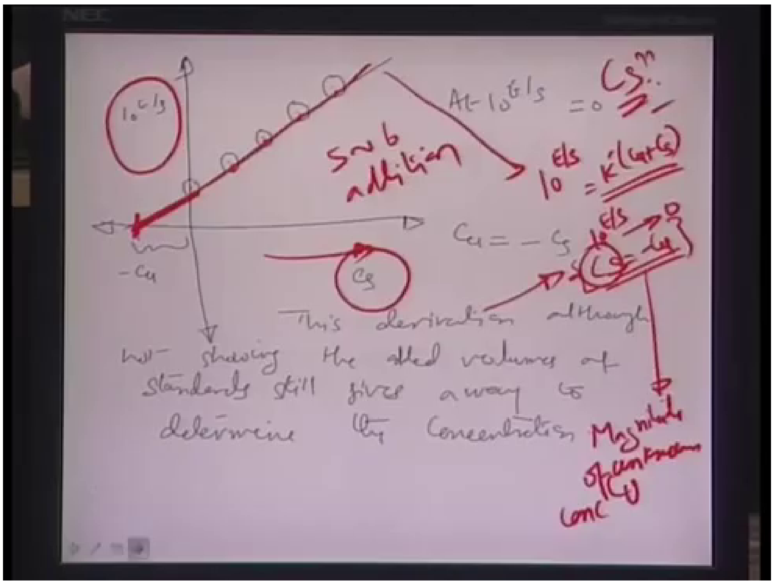

This derivation although not showing the added volumes of standards still gives a way to determine the concentration

So, if you plot that it would be a straight line as we found out last time. So, this essentially is a plot 10 to the power of E by S and the standard concentration Cs. And you can find, out let us suppose we have made 5 or 6 such additions, 5 to 6 additions and each time you measure what is the u emf and the differential of the emf and you plot this straight line based on this several points which come as observation points between $10^{\frac{E}{S}}$ and Cs. So, if we just look at to the equation slightly differently equation, here equation 2 is 10 to the power of E by S equals K dash times of Cu plus Cs. So, what happens when $10^{\frac{E}{S}}$ becomes 0.

So, essentially this you are extending the line all the way back to a point here where $10^{\frac{E}{S}}$ S is 0. So, this would correspond to a concentration of these minus C. Now, the minus really does not have any physical meaning here except the fact that we can actually gage the magnitude of the unknown concentration Cu by looking at the standard edition differentiation Cs. So, it is all about how to calculate Cs which is important is particular case. So, you know the essentially we have to find out a way of determining Cs in such cases and I am going to take the numerical problem where exactly the same thing could be done.

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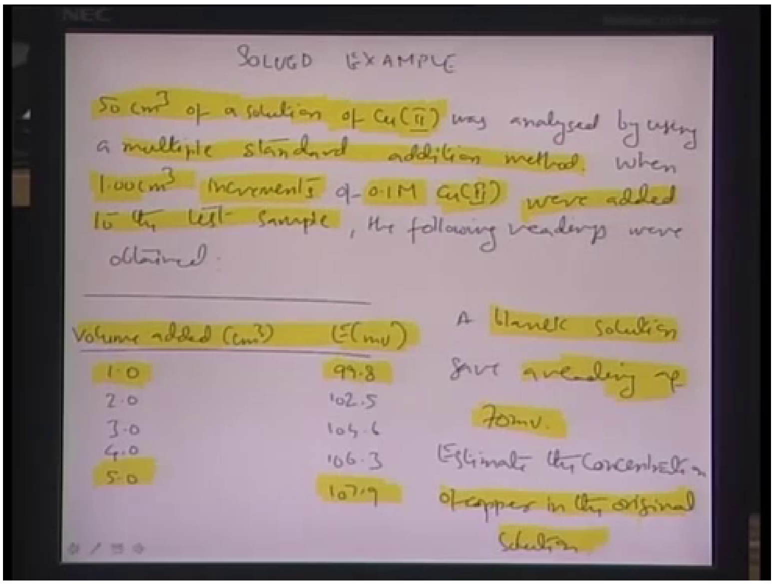

SOLVED EXAMPLE

50 cm^3 of a solution of Cu(II) was analysed by using a multiple standard addition method. When 1.00 cm^3 increments of 0.1 M Cu(II) were added to the test sample, the following readings were obtained.

Volume added (cm^3)	E (mV)
1.0	99.8
2.0	102.5
3.0	105.6
4.0	106.3
5.0	107.9

A blank solution gave a reading of 70 mV.

Estimate the concentration of copper in the original solution.

So, in this problem, as we see we have the 50 centimeter cube of a solution. So, the result copper plus 2 you know salt solution of copper, the corpus state. And this was analyzed by using multiple standard edition method of the Gran plot method. And when it is found that when 1 centimeter cube increments that means, every time the volume added to the standard concentration is 1 centimeter cube. So, 1 centimeter cube increments of point 1 molar Cu 2 is added. So, point 1 molar is basically the value of the known concentration, the standard concentration of the drift solution. They were added to the test sample and there emf readings with taken.

So, the table here represents relationship between the volumes that are added and the corresponding emf that happens because of that. So, if you add one centimeter cube of volume of a Cu plus 2 0.1 molar solution to the 50 centimeter cube of a solution with the original solution, the emf obtained is 99.8 mille volts and this goes all the way up to about 5 increments. So, every times you are adding 1 increment in each particular instances, 1 becomes 2 overall volume, 2 becomes overall volume, 3 becomes overall volume, 4 and so on and so forth.

So, when you have added at the end of the day end of the 5 increments the volume 50 k centimeter cube gets increased 5 centimeter cube. The emf found out to be in that case is 107.9 milli volts. So, if we assume that the blank solution that means, you know essentially the solution which have the unknown concentration of the analyte that gave the reading of 70 mille volts then, we essentially have to estimate the concentration of copper in the origin solution. So, this is again a simple problem just on the Gran plot method. Let us just see or look into the solution aspect.

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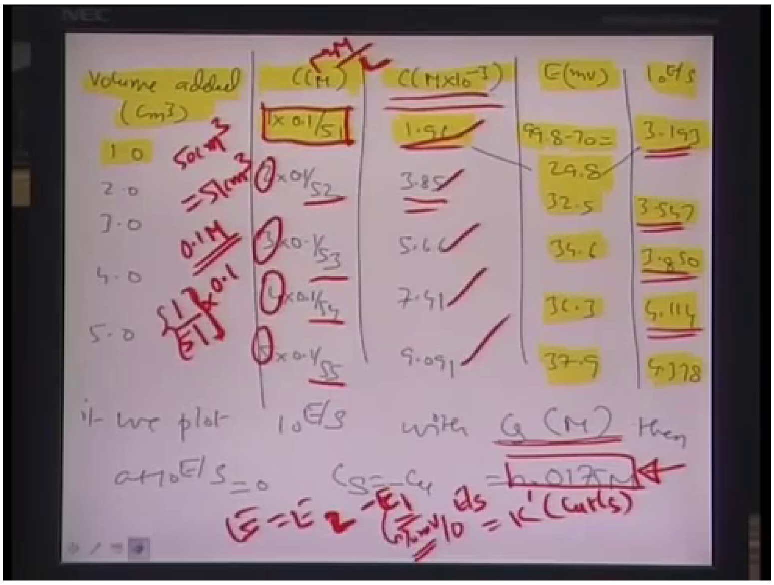

Volume added (cm^3)	C(M)	C(M×10^{-3})	E(mV)	$10^{E/S}$
1.0	1×0.1/51	1.96	99.8-70= 29.8	3.199
2.0	2×0.1/52	3.85	32.5	3.547
3.0	3×0.1/53	5.66	34.6	3.850
4.0	4×0.1/54	7.41	36.3	4.114
5.0	5×0.1/55	9.091	37.9	4.378

if we plot $10^{E/S}$ with C_s (M) then

at $10^{E/S} = 0$ $C_s = -C_x$ = 0.0175 M

E = E2 − E1

S = K'(curls)

So, if you look at, let say we have drawn an alternate table here where, we put the volume added in 1, in centimeter cube in incremental volume. Let us see what is the concentration change because of this addition a 0.1 molar concentration, 1 centimeter cube addition every time and talking terms of how many mille molar concentration increase happens because of this addition. And then, in the fourth column we also note down the various emf's with respect to the blank concentration.

So, if you remember in the equation for the Gran plot, you are talking about term $10^{\frac{E}{S}}$ in the left side. And essentially, this E is nothing but E 1 or E 2 minus E 1. So, E 1 essentially is the is the blank solution emf or the solution which has the unknown concentration, the emf generated by it. So, it has been given in the equation that this emf is 70 milli volts that is the part of the question. So, essentially we are a trying to just calculate this E difference between

E 2 and E 1 and if E 2 is 99.8 as has been given earlier E 2 is 99.8 centimeter cube sorry mille volts. Then, the difference between E 2 and E 1 is written here E as 29.8 mille volts.

Similarly, this goes true for all the different other readings which have been mentioned in the earlier table. We also compute assuming that you know the S to be 59 mille volts, you know per decade. So, essentially we are assuming 1 electron actually, it is 2 electron transfer process because it is Cu plus 2 states. So, we assume 2 electron transfer process. So, that would come 29.5 mille volts. So, you divide this E that is obtained in the earlier column here by S value which is 29.5 mille volts and you obtain $10^{\frac{E}{S}}$ in this manner as these different entries. So, once you do that you are left with the 10 to the power of E by S value, you are also left with the concentration. And let us now explore how the concentration difference is calculated here.

So, if you add 1 centimeter cube of solution to 50 centimeter cube of the parent solution. So, you have 50 centimeter cube of the parent solution and you are adding 1 centimeter cube to so, the total volume would be 51 centimeter cube and you are adding 0.1 molar solution which means, that you essentially adding 1 by 51 times of fraction of volume of 0.1 molar. Molar, if you remember is moles per meter and here essentially talking about volume fraction of the new solution with the respect to the old solution so that we can consider as the fraction of the liter in which 0.1 moles are existing. So, effectively the number of a moles which are added here because of this addition comes out to be 1 times of 0.1 by 51. As you keep on increasing you have 2 centimeter cube by 3 centimeter cube, 4 centimeter cube, 5 centimeter cube.

So, essentially the total volume changes every time 52, 53, 54, 55 and therefore, the number of moles added each time are different on the ratio of 2 times 0.1 by 52, 3 times 0.1 by 1 by 53, 4 times 0.1 by 54 so on and so forth. So, you are obtaining essentially the molar concentration here and then, trying to find out what is number of mille moles and. So, essentially this mille molar concentration is represented here. So, essentially when you talk about this Gran plot, you have to plot the concentration verses of the x access 10 to the power of E by S on the y access. I am not going to show you the plot here but essentially when you take that plot and try to find out the corresponding concentration at the value $10^{\frac{E}{S}}$ equal to 0, for the 0 reading of the y axis it comes out to be 0.0175 molar. So, that is how you can actually use the Gran plot to an advantage to gage the unknown. So, this is also the concentration of unknown solution of the analyte Cu plus 2 50 centimeter of cube which have been taken at the outset in this particular experiment. So, this is way you actually calculate the unknown concentration using the Gran plot method.

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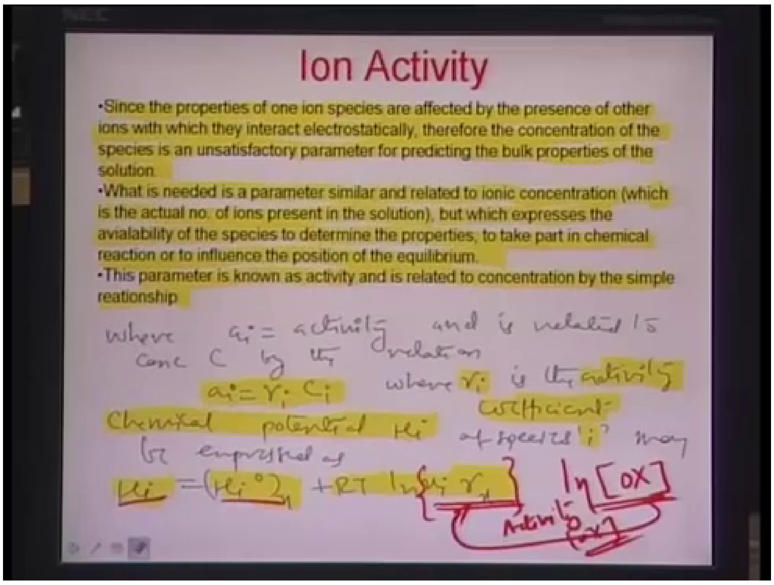

Ion Activity

- Since the properties of one ion species are affected by the presence of other ions with which they interact electrostatically, therefore the concentration of the species is an unsatisfactory parameter for predicting the bulk properties of the solution.
- What is needed is a parameter similar and related to ionic concentration (which is the actual no. of ions present in the solution), but which expresses the avialability of the species to determine the properties, to take part in chemical reaction or to influence the position of the equilibrium.
- This parameter is known as activity and is related to concentration by the simple reationship

where a_i = activity and is related to conc C by the relation

$a_i = \gamma_i C_i$ where γ_i is the activity coefficient of species 'i'

Chemical potential μ_i may be expressed as

$\mu_i = (\mu_i^\circ)_1 + RT \ln\{a_i \gamma_i\}$ $\ln[ox]$

activity [ox]

Let us now take you to a very interesting you know parameter the Ion activity and I have been talking about in this half an hour and last lectures where, we actually see that in many cases specially, in micro devices on the solution volume considered is a very small. It is essentially a big deal if there are more than one participating ions and there sometimes the concentration term really gets kind of reintroduced as fraction of the concentration which is participating for the electron exchange process and that is very obvious because there are interactions between this other ions which are around the ion of interest.

There are forces of attraction and repulsion, definitely there is going to be some kind of a change because of that. So therefore, if you know in such a situation it is a kind of advisable that you find out or you replace the concentration with term called activity, an ion activity. And essentially, we can in a more proper manner define ionic activity as you know this is the properties of 1 species are affected by the presents of other ions which they interact electrostatically with the specious of interest. Therefore, the concentration of the species in an unsatisfactory parameter for predicting the bulk properties of the solutions. So, what is needed is a parameter similar and related to the ionic concentration but then, which is the actual number of ions present the concentration is of course, actually number of percent the solution.

But, this parameter that you are actually talking about is essentially something which is expresses the availability of the species to determine the properties to take part you can chemical reaction and to influence the position of the equilibrium. So, we are talking about when there are completing species the equilibrium really not is the actual case when the there is a single concentration on this species which is available. There in fact, multiple concentrations in this case and therefore, it is very natural to assume that what place an important role is the reduced concentration of effective concentration of the ions which are participating in the reaction. So, this parameter is also known as the activity of a particular species alright. So, it is essentially a factor.

So, essentially instead of the ci the concentration of the species we replace the ci by another parameter ai the activity which is equal to gamma i times of ci. Gamma i is of course the activity coefficient here and ci is the concentration of the ion ith term and that is what essentially it is. So, the chemical potential which is also the grips free energy of a particular system, let say it is mu i and delta g whatever the ith species, it can be represented as delta i 0, mu i 0 times of rt ln xi times gamma x. Now, as you see here what is important for me to tell you here is that this term here which is actually nothing but if you had looked into the earlier, you know earlier derivations etc this was the concentration of the oxidant has been replaced by the activity of the oxidant of the ionic species. So, definitely there is going into the some kind of a chain in the overall way that emf is formed and the overall way that delta g is estimated because of this.

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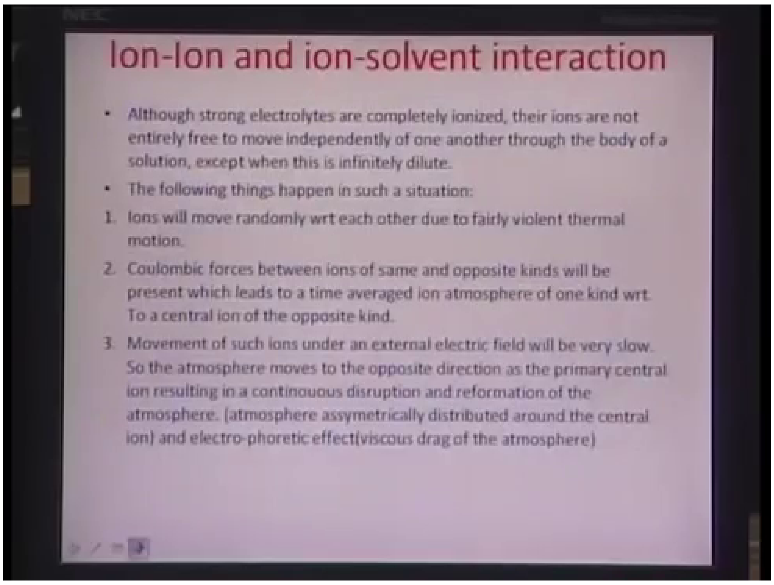

Ion-Ion and ion-solvent interaction

- Although strong electrolytes are completely ionized, their ions are not entirely free to move independently of one another through the body of a solution, except when this is infinitely dilute.
- The following things happen in such a situation:

1. Ions will move randomly wrt each other due to fairly violent thermal motion.
2. Coulombic forces between ions of same and opposite kinds will be present which leads to a time averaged ion atmosphere of one kind wrt. To a central ion of the opposite kind.
3. Movement of such ions under an external electric field will be very slow. So the atmosphere moves to the opposite direction as the primary central ion resulting in a continouous disruption and reformation of the atmosphere. (atmosphere assymetrically distributed around the central ion) and electro-phoretic effect(viscous drag of the atmosphere)

Let us actual look what will happens when you pick, you know the reason with various ions as positive as well as negative. And essentially, in terms of ion or ion solvent interaction there are lots of events which happen. Once you have such a combination of ions and you have electric field which is you know trying to separate these ions. So, what are the main mechanisms of movement of ions 1, mechanism is the violent thermal motion right. Ions have almost always so called random walk process because of thermal energy which is inherent to any system and these ions would kind of walk randomly within the solution that is one kind of a motion. Then, there are coulombic forces between the ions of same or opposite kinds, opposite pole attract each other same of course repel each other. But, then there are such coulombic forces which would predominate, you know the motion of such some kind of ions and essentially this would the coulombic forces between ions of same and opposite kinds will be present which leads to a time average, time atmosphere of 1 time with respect to the other.

So, suppose there is central ion which is, let say positive ion and you have cloud of negative ions rounded. So, these would result into a time average the effect because the forces are continuously happening inside the solution. So, under an electric field there would be tendency of this counter and cloud to go towards the negative electrode because the components positive in this case and the ion of interest which is the negative is going towards the positive electrode and that case what happens is that is kind of nearing. So, the ion cloud tries to move away from the main ion of interest and then there are several such clouds as these ions clutter around from one cloud to another there would be a change in the central ion. So, it is a completely random process. And then, there is also a viscous drag that whenever there is such kind of a unidirectional flow of materials of charges there is also a viscous drag because of this because they are in the fluids of the different ions with respect to the surrounding.

So, if we try to model something where we can really get an estimate of what is the participation level of the independent ion. And in that case it is a very difficult module, I mean kinematically or dynamically if you are able to investigate it is one of the great things. So, since from 1923 onwards we do have a model and that is exactly is what I want to point out here, just give me a; that until 1923 the activity coefficients was really experimentally predicted and that was almost always the case. There was no other means to accurately find the activity coefficient. But, then in 1990, I mean 1923 there was a mechanism which was gone out in terms of certain set of equations called Debye-Huckel equations and Debye-Huckel theory which would be able to predict the activity using all these different constants constraints about ion and ions sulfite are in interaction that I talked about the last slide. So, let me try and you know give you an idea of how we can predict the activity of an ion mathematically from looking at the dynamics in the kinematics of such reaction.

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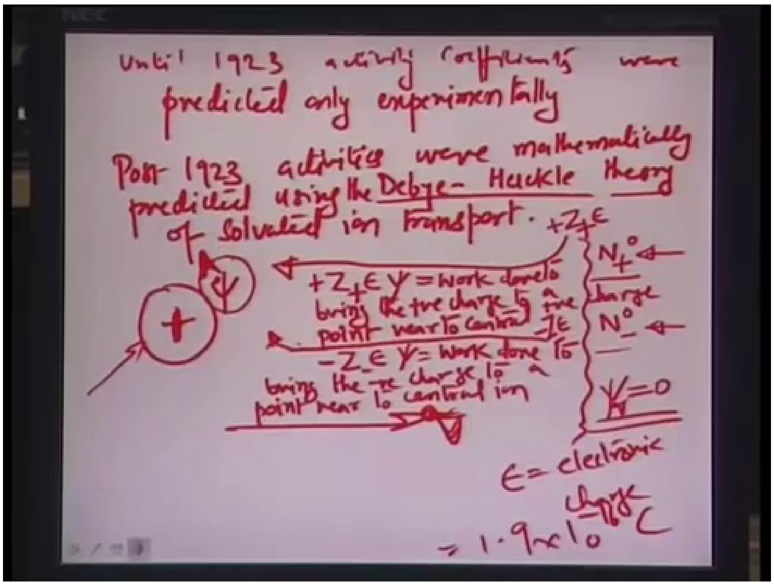

Until 1923 activity coefficients were predicted only experimentally

Post 1923 activities were mathematically predicted using the Debye- Huckle theory of solvated ion transport.

$+Z_+\epsilon\psi$ = work done to bring the +ve charge to a point near to central ion

$-Z_-\epsilon\psi$ = work done to bring the -ve charge to a point near to central ion

ϵ = electronic charge $= 1.9 \times 10^{-16}$ C

So, until 1923, the activity coefficients were predicted only experimentally. Post 1923, the activities were mathematically predicted using the Debye-Huckle theory of solvated ion transport. So, let us suppose and I am actually going to derive this. Now, I am just going to derive how we can predict the activity. So, let suppose there is a positive ion here and there is a potential file somewhere closed to this ion and potential by potential we mean that is the you know essentially it is a basically per unit field length. So, there is almost always field time's length. So, essentially the electric field is a nothing but the gradient of the potential. So, there is potential around this central ion which exists. Let us suppose that at infinity distance from this ion there is a distribution of charge of plus and minus kind per centimeter or per unit volume. So, n plus 0 and n minus is 0.

So, essentially we are talking about there is a ion of interest here, as you see in this particular case there is a potential very close to the ion and there is a distribution of a positive and negative ions at a distance infinity from this central positive ion of interest. So, we want to find out the amount of work that would be done in order to transfer a small amount of charge from infinity to this point here, which has a potential 5 and as you know we can safely assume that potential is also inversely related to you know to essentially the distance. So, therefore, infinity the potential is 0. So, there is no potential due to this ion is positive ion of interest and this distance infinity from it. So, if I want to bring in some positive charge, let say with a valency Z plus. So, what would be the charge if we assumed, if silent to be the electron electronic charge 1.9×10^{-16} coulomb. So, essentially we are talking about z plus times of epsilon. And let us suppose this is the amount of positive charge and minus z minus epsilon is the amount of negative charge. So, the amount of work which would be done in order to bring this charge add a 0.5 would be nothing but plus z plus epsilon, if I write this is the amount of work which is done to bring the positive charge to a point near to the central positive charge. Similarly, in order to bring the negative charge near to this 0.5, the amount of work we should be done is negative z minus epsilon phi.

So, this is the work done to bring the negative charge to a point near to central ion. Of course, you have to be positive work in order to bring the positive charge to the positive center and automatically the negative charge it come by attraction onto the positive center. So, you basically the system will automatically do the work. So, this part is very clear right; that what happens in the near vicinity of the positive charge. So, now let us look at what really is going to be the distribution near such a point. Let us call this point a let's call particular point near this where the phi is the potential as the point a alright.

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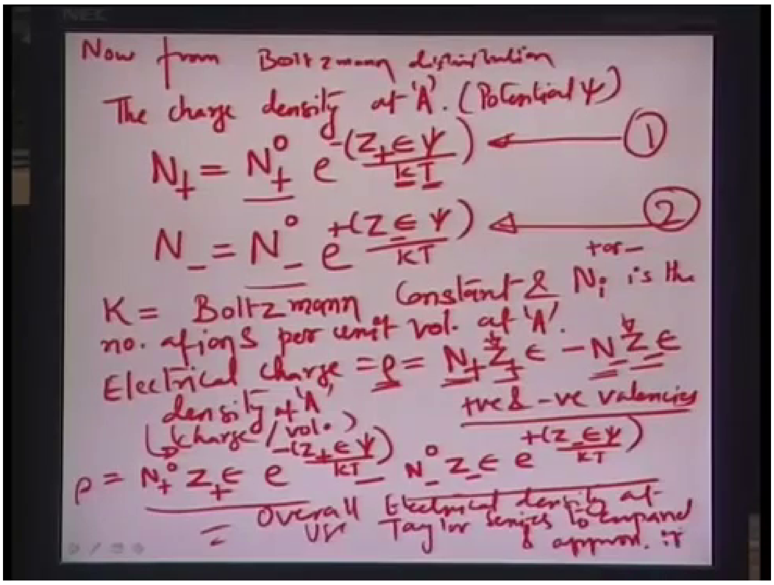

Now from Boltzmann distribution

The charge density at 'A'. (Potential ψ)

$$N_+ = \underline{N_+^0}\, e^{-\left(\frac{Z_+ \epsilon \psi}{KT}\right)} \longleftarrow ①$$

$$N_- = \underline{N_-^0}\, e^{+\left(\frac{Z \epsilon \psi}{KT}\right)} \longleftarrow ②$$

for −

K = Boltzmann Constant & N_i is the no. of ions per unit vol. at 'A'.

Electrical charge density at 'A' (charge/vol.) $= \rho = \underline{N_+ Z_+ \epsilon} - \underline{N_- Z_- \epsilon}$

+ve & −ve valencies

$$\rho = N_+^0 Z_+ \epsilon\, e^{-\left(\frac{Z_+ \epsilon \psi}{KT}\right)} - N_-^0 Z_- \epsilon\, e^{+\left(\frac{Z_- \epsilon \psi}{KT}\right)}$$

= Overall Electrical density at

Use Taylor series to expand & approx. it

$+\epsilon\psi$

$Z_❑$

¿ −

¿+❑^{0} $e^❑$

+¿ $N_❑$

$N_❑$

$-\epsilon\psi$

$Z_❑$

¿+¿

−❑^{0} $e^❑$

−= $N_❑$

$N_❑$

$-\epsilon$

$-Z_❑$

$+\epsilon - N_❑$

$+Z_❑$

$\rho = N_❑$

$+\epsilon\psi$
$Z_{❑}$
$¿\frac{❑}{kT}$
$¿-\epsilon\psi$
$Z_{❑}$
$¿+¿$
$-e^{❑}$
$-$
$¿+e^{❑}$
$+Z_{❑}$
$\rho=N_{❑}$

So, at a let us compute what is the charge distribution at a given, the charge distribution at infinite distance from this charge. So, this also known as you know it is also given from the Boltzmann’s distribution. So, without going into the details of what Boltzmann distribution is on, I am simply going to write that form Boltzmann distribution the charge density at a, remember the point a at which the potential was phi in the last slide. So, the positive charge distribution will be given by looking at the positive charge distribution at infinity times exponential to the power of minus zeta plus epsilon phi by KT. So, this is essentially is the work done by KT. K is the Boltzmann constant and T is the ambient temperature around the point a or at which the point a is existing.

Similarly, the negative charge density is also related to the negative charge density as infinity times E to the power of plus Z minus epsilon phi by KT. One has to assume that, this is a self-driven process, this is a temperature dependent process. So, if you have a temperature t, it automatically means that you know there can be a relationship between without doing any external work of course, there is a relationship between you know the density at the charge density at infinity and the charge density at the point a at which the potentials is phi. So, they just for the sake of clarity, K is also called the Boltzmann constant. And the particular n here let me call N i whether it has positive or negative is the number of ions per unit volume number of ions per unit volume at a.

So, really the electrical density at A can be current represented as N plus Z plus epsilon right minus N minus Z minus epsilon. Remember, Z plus and Z minus are the positive and negative valencies. Why we need valencies because when we are talking about ion transport there has to be an idea of whether is a negative ion or a positive ion what is going to be the total amount of charge electronic charge that ion contains. So, therefore Z plus or Z minus essentially very very important to be included in the equation because they are function of any ions oxidation and reduction state. So, the total charge density that means, charge per unit volume. This is charge per unit volume row is given by N plus Z plus e minus N minus Z minus e. So, from equations here 1 and 2, we can substitute what is the values of N plus and N minus and write the final charge density row as a equal to N plus 0 Z plus epsilon e to the power of minus Z plus epsilon phi by KT minus N minus 0 Z minus epsilon e to the power of plus Z minus epsilon phi by KT.

So, we have in the final electrical charge density has you know simply a difference others between the N plus 0 Z plus epsilon and minus 0 Z minus epsilon e to the power of minus Z plus epsilon phi by KT into the power of plus Z minus epsilon phi by KT. So, that is in the overall electrical density at a, the electrical density at a. So, let use tailor series to expand this a little bit and also to approximate it.

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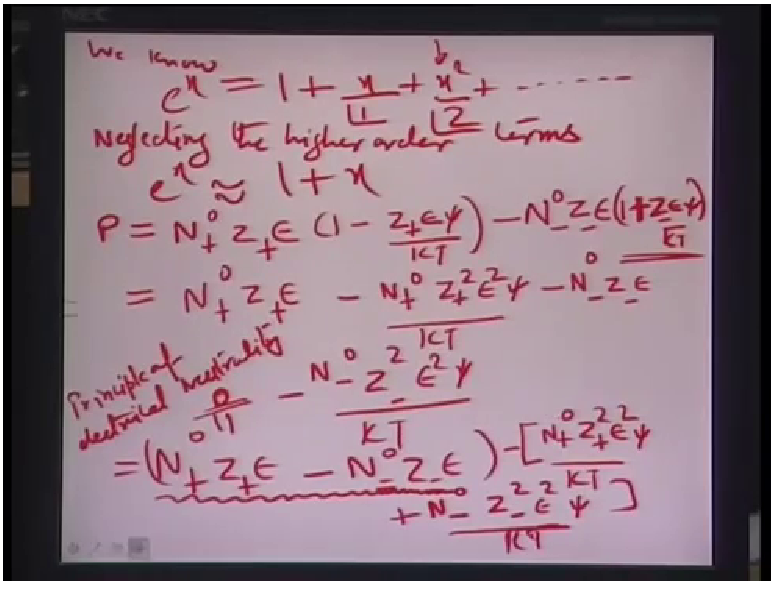

We know

$$e^x = 1 + \frac{x}{\lfloor 1} + \frac{x^2}{\lfloor 2} + \cdots$$

Neglecting the higher order terms

$$e^x \approx 1 + x$$

$$\rho = N_+^0 Z_+ \epsilon \left(1 - \frac{Z_+ \epsilon \psi}{KT}\right) - N_-^0 Z_- \epsilon \left(1 + \frac{Z_- \epsilon \psi}{KT}\right)$$

$$= N_+^0 Z_+ \epsilon - \frac{N_+^0 Z_+^2 \epsilon^2 \psi}{KT} - N_-^0 Z_- \epsilon - \frac{N_-^0 Z_-^2 \epsilon^2 \psi}{KT}$$

Principle of electrical neutrality

$$= \underbrace{\left(N_+^0 Z_+ \epsilon - N_-^0 Z_- \epsilon\right)}_{0} - \left[\frac{N_+^0 Z_+^2 \epsilon^2 \psi}{KT} + \frac{N_-^0 Z_-^2 \epsilon^2 \psi}{KT}\right]$$

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \ldots = 1 + x$$

$$e^x = 1 + x$$

$$\begin{gathered}
\frac{Z_{+\in\Psi}}{KT} \\
1- \\
\text{¿}\frac{Z_{+\in\Psi}}{KT} \\
1+\text{¿}-\in \\
-\square^{0} Z_{\square} \\
+\in \\
+\square^{0} Z_{\square} \\
P=N_{\square}
\end{gathered}$$

$$\begin{gathered}
-\square^{0}\frac{Z_{-}^{2}\in^{2}\Psi}{KT} \\
N_{\square} \\
-\in- \\
-\square^{0} Z_{\square} \\
\frac{Z_{+\text{¿}^{2}\in^{2}\Psi}}{KT}-N_{\square} \\
+\square^{0}\text{¿}\,N_{\square} \\
+\in- \\
+\square^{0} Z_{\square} \\
P=N_{\square}
\end{gathered}$$

So, as we know from a you know elementary mathematics, that if use Tailor series in such a situation; you can have e to the power of x being predicted by 1 plus x by 1 factorial plus x square by 2 factorial plus so and so forth ok. So, neglecting in the higher order terms, we are left with an estimation of e to the power x as 1 plus x. If assume x to the small enough we can really safely ignore the higher orders. If you look at the equation, we predicted in the earlier you know expression here, we have this important factor epsilon which is 10 to the power of minus 19 and you know e by K also is a probably going to be in a very small order. And therefore, the overall term Z plus epsilon pi by KT is a really you know it is really very small and it is significant. And therefore, the higher orders of such a term and safely neglected in the equation.

So, if you put this back in to our earlier equation here, on charge density the density of charge rho would come out to be equal to N plus 0 Z plus epsilon times of 1 minus Z plus epsilon pi by KT. So, basically as the talking the charge density here is a essentially given by N plus 0 Z plus epsilon 1 minus Z plus epsilon pi psi by KT; from the Tailor approximation and this is the positive density. And the negative density is minus N minus 0 Z minus epsilon 1 minus Z minus epsilon pi by KT. So, essentially there is how you indicate both you know the plus as well as the minuses. And so when we are talking about, so this is really the overall charge density also which we are investigating.

So, if we just open the brackets and trying to do a little bit of simplification here, we are left with N plus 0 Z minus epsilon minus N plus 0 Z sorry, Z plus epsilon minus N plus 0 Z plus square epsilons square pi by KT alright; minus N minus 0 Z minus epsilon plus N minus 0 Z minus square epsilon square psi by KT. So, basically I am sorry this was actually a plus because if you go back here, if you look at what the density is. Is essentially e to the power of Z minus epsilon pi by K and this was a little type where here well writing this. This will be 1 plus x, 1 plus Z minus epsilon pi and K T. Resulting in this sign here to be changing into minus. So, let us just rearrange the terms that we have so far, and then we are left with N plus 0 Z plus epsilon minus N minus 0 Z minus epsilon as one bracket; and minus of this whole other term you know N plus 0 essentially Z plus square epsilons square pi by K T and plus N minus 0 Z minus I am sorry.

As a due to the, you know space consideration let us write this term of the of the bottom here. So, we left with the second term here, which is give me minute. Plus N minus 0 Z minus square epsilons square pi by KT bracket closed. So, there are several interesting things to be shared here. One is that this particular term which we are talking about here has to be 0, and why that is so as that? This is also the principle of electrical neutrality, principle of electrical neutrality.

Now, I just need to explain why that is. So, so this principle essentially states that if you talking about you know positive and negative charges in a certain solution, there is automatically you know chance of these to be redistributed in the manner. So, that the overall medium is electrical neutral. So, there should be equal number of positive and equal number of negative charges and there extend. So, here when we are talking about the charges that infinity placed from this point the central ion which is a positive ion. The total amount of charge that we are talking in terms of you know let say the valency on the positive charges Z plus, the valency on the negative charges Z minus; and the distribution of the charges per unit volume at infinity is N plus 0 and n minus 0. So, really in the total positive charge that we have at infinity permanent volume is N plus 0 Z plus times of epsilon, epsilon being the electronic charge and the total amount of negative charge that we have at infinity from this point A where the potential is pi is N minus 0 Z minus epsilon. So, they should be exactly equal and opposite or in another words the summation of the charge as should be 0. Are the medium in general should be electrical neutral. So, therefore, in the first term here really is a 0 term. It is a total you know that is the absolutely no charger, it is a neutral charge. The second term here is essentially of importance to us because that in a sense is what the charge density really is and let us actually write it down next slide.

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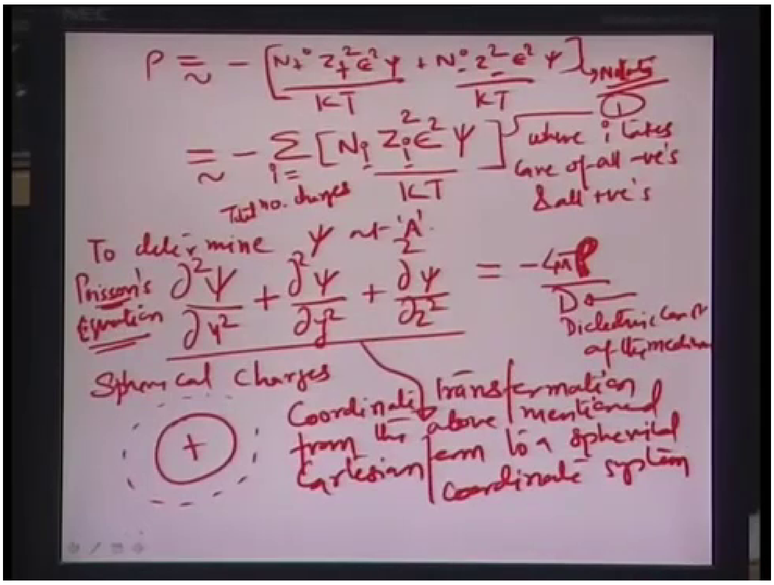

$$-\square^{0}\frac{Z_{-}^{2}\in^{2}\Psi}{KT}$$

$$N_{\square}$$

$$\frac{Z_{+¿^{2}\in^{2}\Psi}}{KT}+¿\,N_{\square}$$

$$+\square^{0}¿$$

$$P\cong-$$

$$\cong-\left[\frac{N_{i}^{0}Z_{i}^{2}\in^{2}\Psi}{KT}\right]$$

$$\frac{\partial^{2}\Psi}{\partial x^{2}}+\frac{\partial^{2}\Psi}{\partial y^{2}}+\frac{\partial^{2}\Psi}{\partial z^{2}}=\frac{-4\pi P}{D\sigma}$$

So, the second term rho effectively becomes minus N plus square and N plus 0 Z plus square epsilon square pi by KT, plus N minus 0 Z minus square epsilon square pi by KT. What is interesting here to be see is that, we can actually note this in slightly different way. So, what I am doing now is really not from the stand point from algebra, but from the stand point of notation. The idea is that is this notation is continue just for convenient say throughout the equations and we do understand what it means that the end of the day. Then we are very clear about what has to be done. So, I would say that this thing be represented by sigma Ni Zi square epsilon square pi by KT. Where, the notation is such that i takes care of all negatives and all positives, positive charges in the medium.

So, i something which is a generic subscript which if we were to actually take all these ions together and number them as 1, 2, 3, 4 so on. Whether it is positive or negative or irrespective of whether it is positive or negative. Then we are actually having i number of ions in the solution and therefore, whether it is a you know a plus charge density you know plus positive valency or whether it is a negative charge density negative valency can be sub scripted by the subscript i as you can see here, in this particular you know equation. So, we are left with the charge density approximately to be Ni sigma, Ni Zi square epsilon square pi by KT; where i is the number of the total number of charges irrespective of whether it is positive or negative charge. So, all set in done, let us actually call this equation, equation number one for a whether sake of convenience.

So, let us now look at a little different aspect, as to what this electrostatic potential pi would be or how we can calculate the electrostatic potential pi. You know add the point A near the positive ion. So, let us say that we want to determine in the pi at A. So, one way of doing that would be by using the Poisson's equation which gives a special relationship of the potential function around a charge a with respect to the density of the charge which is available at that particular point. So, we can write it write the Poisson's equation, and I am really not going into details of how the Poisson's equation is derive because that is a essentially going to be the curriculum for a you know second year graduate course and mathematics. But essentially we would like to use this equation and try to solve for the potential function pi, in interest of our finding out the overall activity of an ion or ion species. So, we have the double def derivative of a pi with respect to x plus the double partial derivative of a psi with respect to y plus the double partial derivative of pi with respect to Z the potential function is the pi of the psi.

That essentially can be equated to the overall charge density and the dielectric constant D of the medium this, these essentially the dielectric constant of the medium. Ability of medium also to give way to or store charge. So, this is the dielectric constant of the medium. And so essentially the Poisson's equation is a relationship between the variation of a potential function with respect to all the three coordinates and it gives a relationship between that variation and the charge density of an atmosphere of which the pi is to be considered off.

So, in the first thing we would like to do is because you talking about spherical charges. You would like to a transform you know the coordinates of this particular equation into the spherical coordinates; so we are considering spherical charges. If you may remember we would talking about the positive charge which is spherical and the atmosphere around this particular charge. So, essentially we would do a coordinate transformation from the above mentioned Cartesian form; this one right? To a spherical coordinate system. So, in order to do that I would just like to illustrate how you would be able to change this, but then I, it is expected that you basically you know, in one of the homework assignments I would give you later on. Do and show the derivation and this can be this is available in any of the as I told you before first or second your graduate text book on elementary engineering mathematics ok. So, let us look at how this coordination transformation would be done.

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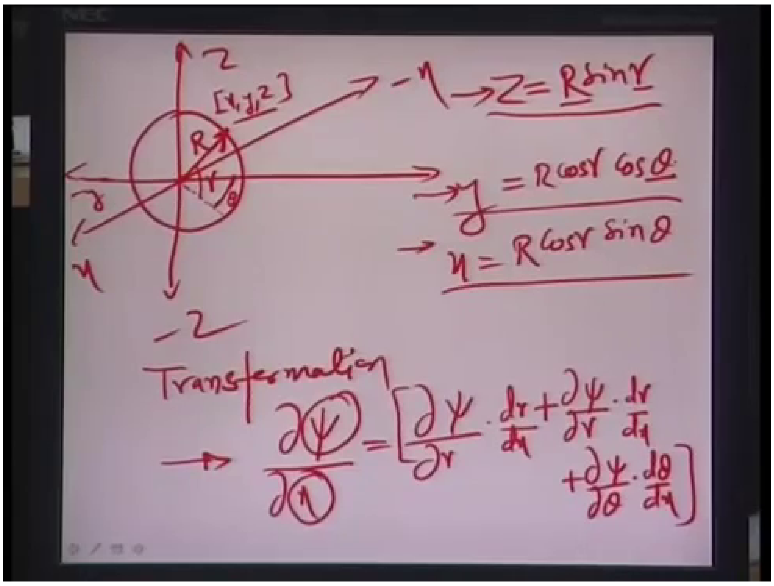

$$\frac{\partial\Psi}{\partial x}=\left[\frac{\partial\Psi}{\partial r}\frac{dr}{dx}+\frac{\partial\Psi}{\partial r}\frac{dr}{dx}+\frac{\partial\Psi}{\partial\theta}\frac{d\theta}{dx}\right]$$

So, let suppose we have a Cartesian coordinate here; x y z. So, essentially this is the x minus x, this is the y minus y, is z minus z. Now we draws spear here somewhere, in center and we assume that there is a radius vector R. Essentially of this fear projected in the three demotions from it is a center which is the geometrical center x is equal to 0, y is equal to 0, and z is equal to 0. So, let us further assume that we take the projection of this R vector on to the x y plane, alright. So, this is the projection of the R vector on to the x y plane and we assume that the angle between the projection of the R vector on the x y plane and the R vector is gamma; alright. So, automatically this z value comes out to be equal to R sine gamma, alright. So, this is 90 minus gamma, so R sine gamma is the z value.

So, what happens to the x and y value? Let us further assume that essentially you know the projection vector of the R on the x y plane is at an angle theta with respect to the y coordinate. So, in that case the corresponding y value here, corresponding to this radius vector would be equal to R sine gamma cos theta and the x value would be equal to R sine gamma I am sorry, R cos gamma. So, essentially this thing is cos, so also cos. So, R cos gamma, cos theta and R cos gamma sine theta. So, this is what in the y and the x values are. This is essentially nothing but, you know the in the projection of the point x y z at the end of the radius vector with respect to the various angles, that the radius vector makes in the projection on the x y plane and essentially the projection of a on the y in the x coordinate.

So, once these 3 vectors are figured out, you know transforming the coordinates would essentially mean. You have to do d pi by d x as d pi by d r times of d r plus d pi by d times of d x by d r; d x, d r by d x. I am sorry, times of d r by d x plus d pi by d gamma times of d gamma by d x plus d pi by d theta times of d theta by d x. So, essentially this is a actually nothing but a, you know total partial differential of pi with respect to x been access dependent on the various parameters R, you know gamma and theta.

Thank you.