Bio – Microelectromechanical Systems

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Module No. # 01

Lecture No. # 07

Welcome back to the lecture number 7 of this BioMEMS course and essentially would like to do just a quick review of what was covered in the last lecture before trying to begin this new lecture.

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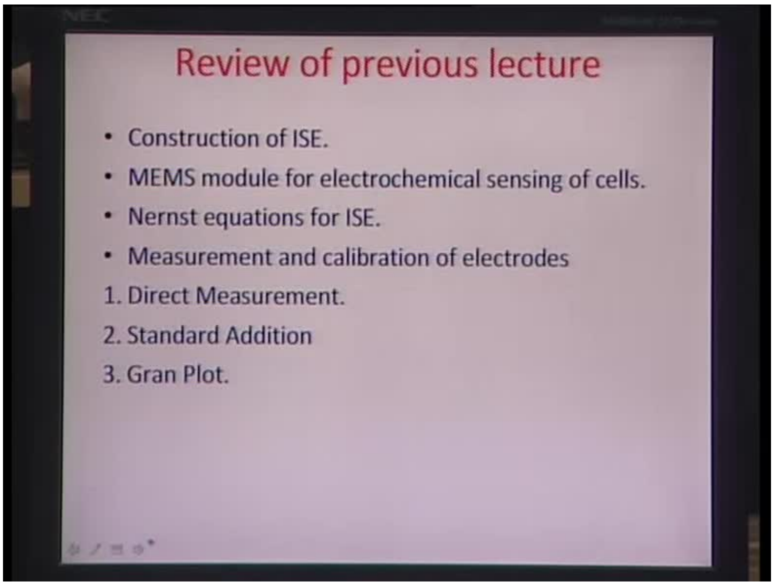

Review of previous lecture

- 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.

In the last session, we discussed at length about the construction of ion selective electrodes. Ion selective electrodes essentially are those electrodes which have a tendency of selecting one or more ions of interest over the bunch of different ions. There are certain modalities which we need to consider before you explore how to construct these. Typically, you have to have a recognition agent or an identifier which can select or which can offer selectivity.

So, one way of doing it, as we learnt last time, is basically preparing a polymer paste like polyvinyl chloride and then trying to include in it some material which is causing the selectivity or selection action. One fantastic example was that of valinomycin, where these are organic extracts available on the cell membrane which can help to basically exchange calcium and potassium ions.

If you want to make calcium selective or a potassium selective electrode, you have to have these valinomycin moieties in a polymeric material. The way you prepare the electrode is that you take a sin glass capillary, you dip it and create a plug kind of a thing which is also like an ion exchange membrane and then basically fill that with a certain electrolyte, and 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 two different oxidant concentrations and that avoided the need for reference electrolyte as has been the case in all the ISEs. We talked and discussed about some MEMS modules for electrochemical sensing of cells wherein we showed the small silicon chip and showed 64 recording channels there, where there could be a single cell by single cell isolation and the electrodes could record the response from those cells etcetera.

Then we tried to derive the famous Nernst equation which is also the equation meant for describing a relationship between the EMF and the log of concentration. We found out that the Nernstian slope is equivalent to a parameter ‘s’ which is essentially 0.059 by n; n 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 certain analyte is known or vice versa. Then we talked essentially about how to measure and calibrate such electrodes and we discussed about two different techniques: direct measurement where in you just find out the EMF for certain concentration using the Nernstian approach and standard addition method where you use a standard concentration and standard volume. Then find out a new concentration and from the two EMFs that you get, you could actually gauge what is the unknown concentration, if the standard concentration in the volume of the unknown solution and volume of the standard solution they are all known.

We were just about to begin to talk about Gran plot. 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 reviewing and then to numerical problem and move ahead.

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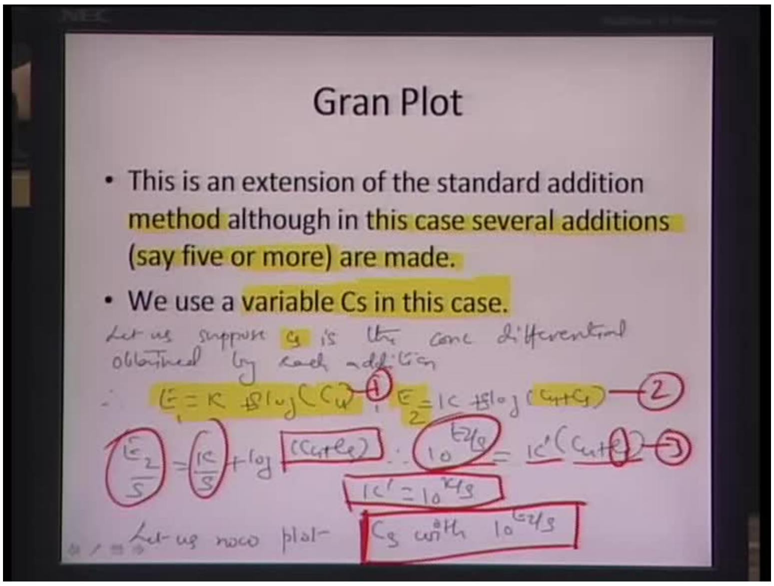

Gran Plot

- 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

$\therefore E_1 = K \pm S \log (C_u)$ — ① ; $E_2 = K \pm S \log (C_u + C_s)$ — 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 $\boxed{C_s \text{ with } 10^{E_2/S}}$

The third method which we slightly discussed last day was the Gran plot. This is essentially an extension of the standard addition method. Although in this case, several additions say five or more are made. So, in this particular method there are several additions of known concentration analyte.

Here we define Cs as a variable in a manner that the Cs essentially is a concentration where it is basically the concentration differential. If you are adding a certain concentration to the unknown concentration of the analyte, the overall concentration that comes out because of this addition of known volumes of the standard and known volumes of the unknown that can be represented as the unknown plus a differential, a concentration differential; so, that differential is Cs. We are just redefining the parameters Cs slightly in a different manner and this should be very clear at the outset because sometimes there is confusion because of that in solving numerical problem.

Let us suppose that Cs is such a concentration and if you talk about an unknown analyte of concentration Cu, you can find out the EMF from this particular equation k plus s log Cu. This is the Nernstian approach to determine the EMF. Let us suppose that after the addition the new concentration becomes Cu plus Cs, Cs being the differential concentration and the new EMF, E2 can be written now as k plus s log Cu plus Cs.

If this is treated as equation 2 here Let us suppose this is equation 1; this is equation 2. The equation 2 can be again redefined as E2 by s equals k by s plus log of Cu plus Cs and therefore, 10 to the power of E2 by s equal to k dash times of Cu plus Cs and k dash essentially here is 10 to the power of k by s.

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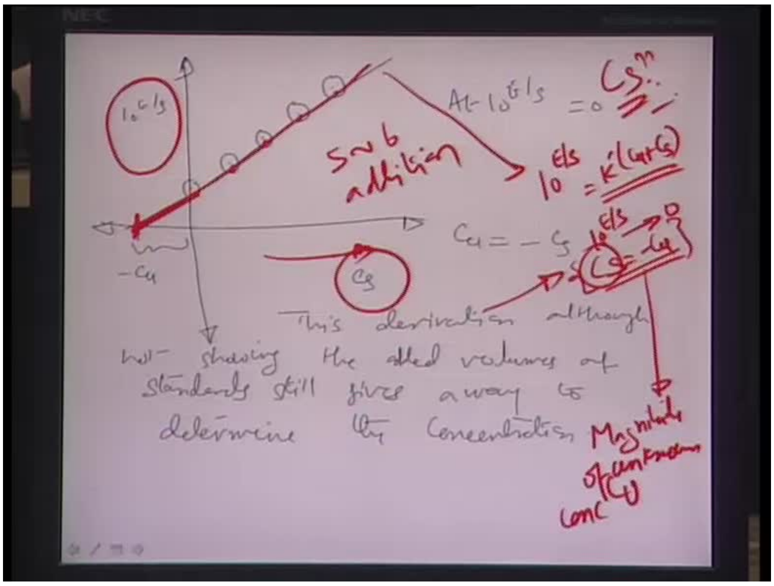

This derivation although not showing the added volumes of standards still gives a way to determine the concentration

Let us now plots Cs with e to the power of 10 to the power of E2 by s. This equation here, equation 3 is just like a straight line. Between Cs and 10 to the power E2 by s the relationship is something like y is equal to m x plus c. If you plot that, it would be a straight line as we found out last time. This essentially is a plot between 10 to the power

E by s and the standard concentration Cs. and you can find out Let us suppose, we have made 5 or six such additions - 5 to 6 additions and each time you measure what is the new EMF and the differential of the EMF. You plot this straight line based on several points which come as observation points between 10 to the power of E by s and Cs.

If we just look at 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. What happens when 10 to the power of E by s becomes 0? So, essentially this you are extending the line all the way back to a point here, where 10 to the power of E by s is 0. This would correspond to a concentration which is minus Cu. Now, minus really does not have any physical meaning here except the fact that we can actually gauge the magnitude of the unknown concentration Cu by looking at the standard addition deferential Cs. So, it is all about how to calculate Cs which is important in this particular case.

So, we have to find out a way of determining Cs in such cases and I am going to take you through a numerical problem where exactly the same thing would be done.

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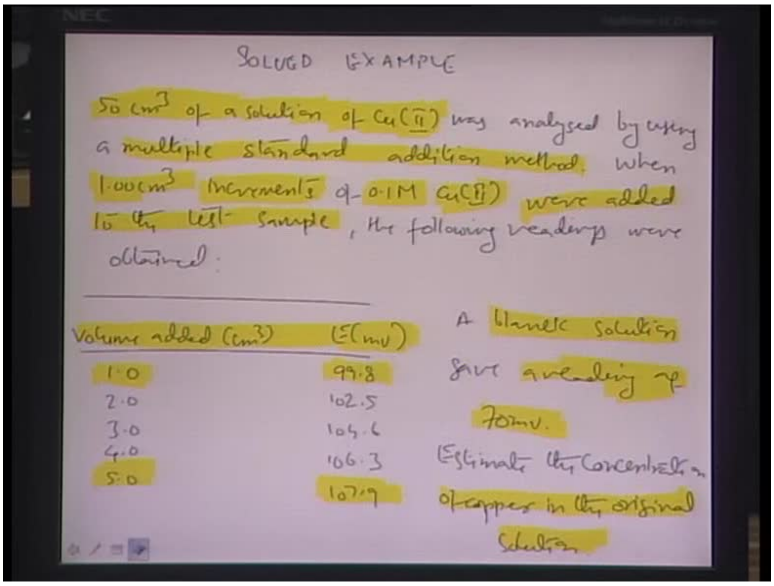

SOLVED EXAMPLE

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	104.6
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.

In this problem, as you see we have 50 centimeter cube of a solution. There is a copper plus 2 salt solution of copper in the cuprous state and this was analyzed by using multiple standard addition method or the Gran plot method. When it is found that when 1 centimeter cube increments means that every time the volume added on the standard concentration is 1 centimeter cube, 1 centimeter cube increments of 0.1 molar Cu(II) is added. 0.1 molar is basically the value of the known concentration of the standard concentration of the additive solution. They were added to the test sample and their EMF readings were taken. The table here represents relationship between the volumes that are added and the corresponding EMF that happens because of that. If you add 1 centimeter cube of volume of Cu plus 2, 0.1 molar solution to this 50 centimeter cube of a solution of the original solution, the EMF obtained is 99.8 millivolts and this goes all the way up to about 5 increments. So, every time you are adding 1 increment in each particular instance, 1 becomes 2 overall volume, 2 becomes overall volume 3, 3 becomes overall volume 4 and so on. So, when you have added, at the end of the day after 5 increments, the volume 50 kills centimeter cube gets increased by 5 centimeter cube, the EMF found out in that case is 107.9 millivolts. So, if we assume that the blank solution that means the solution which had the unknown concentration of the analyte, that gave a reading of 70 millivolts then we have to estimate the concentration of copper in the original solution. This is again a simple problem on the Gran plot method.

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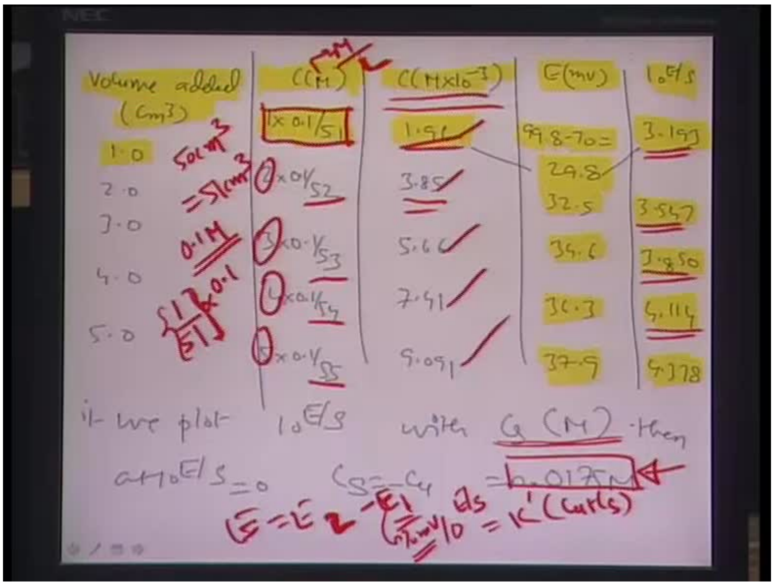

Volume added (cm^3)	C (M)	C ($M \times 10^{-3}$)	E (mV)	$10^{E/S}$
1.0	$1 \times 0.1/51$	1.96	99.8 - 70 = 29.8	3.193
2.0	$2 \times 0.1/52$	3.85	32.5	3.547
3.0	$3 \times 0.1/53$	5.66	34.6	3.850
4.0	$4 \times 0.1/54$	7.41	36.3	4.114
5.0	$5 \times 0.1/55$	9.091	37.9	4.378

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

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

$E = E_2 - E_1$ $10^{E/S} = K'(Cu^{2+})$

Let us just see or looking into the solution aspect. If you look at We draw an alternative table here, where we put the volume added in 1 centimeter cube 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. We talk in terms of how many milli molar concentration increase happens because of this addition and then in the fourth column, we also note down the various EMFs with respect to the blank concentration.

If you remember in the equation for the Gran plot, you were talking about a term 10 to the power of E by s in the left side and this E is nothing but, E1 minus or E2 minus E1. E1 is the blank solution's EMF or the solution which has the unknown concentration, the EMF generated by it. It has been given in the equation that this E1 is 70 millivolts as part of the question.

So, we are trying to just calculate this E difference between E2 and E1. If E2 is 99.8 has been given earlier E2 is 99.8 millivolts, then the difference between E2 and E1 is 29.8 millivolts written here as E . Similarly, this goes true for all the difference other readings which have been mentioned in earlier table.

We also compute assuming s to be 59 millivolts per decade. We are assuming 1 electron actually it is 2 electron transfer process because it is Cu plus 2 state. We assume a 2 electron transfer process and so that would become 29.5 millivolts.

You divide the E that is obtained in the earlier column here by the s value which is 29.5 millivolts and you obtain 10 to the power of E by s in this manner as these different entries. Once you do that, you are left with the 10 to power e by s value; you are also left with the concentration and now let us explore how the concentration difference is calculated here.

If you add 1 centimeter cube of solution to 50 centimeter cube of the parent solution, you have 50 centimeter cube of the parent solution and you are adding 1 centimeter cube to it so the total volume would be 51 centimeter cube and you are adding 0.1 molar solution which means that you add 1 by 51 times of a fraction of volume 0.1 molar. Molar, if you remember is moles per litre. Here you are talking about a volume fraction of the new solution with respect to the old solution and that we can consider as the fraction of the litre in which 0.1 moles are existent.

So, the number of 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 add 1 centimeter cube, you add 3 centimeter cube, 4 centimeter cube, 5 centimeter cube. 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 53, 4 times 0.1 by 54 and so on.

So, you are obtaining the molar concentration here and then trying to find out what is number of millimoles. Essentially, this millimolar concentration is represented here.

When you talk about this Gran plot, you have to plot the concentration on the x axis versus 10 to the power of E by s on the y axis. I am not going to show you the plot here, but then essentially when you take that plot and try to find out the corresponding concentration at the value 10 to the power of E by s equal to 0, for a 0 reading of the y axis, it comes out be 0.0175 molar. That is how you can actually use the Gran plot to an advantage to gauge the unknown. This is also the concentration of the unknown solution of the analyte Cu plus 2, 50 centimeter cube of which have been taken at the outset in this particular experiment. So, this is the way you actually calculate the unknown concentration using the Gran plot method.

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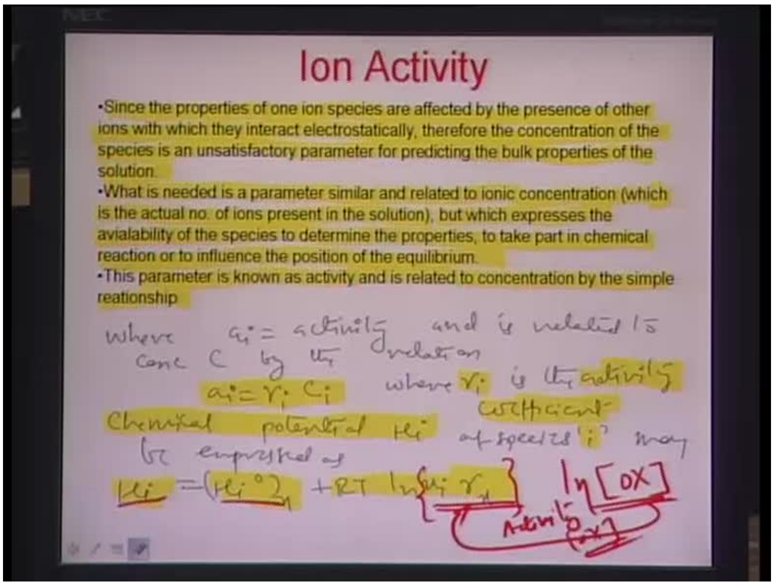

Ion Activity

- 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 me now take you to a very interesting parameter - the ion activity. I have been talking about this half an hour in my last lecture where we actually see that in many cases especially in micro devices when the solution volume considered is very small, it is a big deal. If there are more than 1 participating ions and there sometimes, the concentration term really gets kind of reintroduced as the fraction of the concentration which is participating for the electron exchange process. That is very obvious because there are interactions between these other ions which are around the ion of interest. There are forces of attraction, repulsion and definitely there is going to be some kind of a change because of that.

Therefore, in such a situation it is kind of advisable that you find out or you replace the concentration with a term called activity - an ion activity. We can in a more proper manner define ionic activity as the properties of one species are affected by the presence of other ions, which they interact electrostatically with the species of interest. 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 the ionic concentration, but then which is the actual number of ions present? The concentration is of course, the actual number of ions present in the solution, but this parameter that we are talking about is essentially something which expresses the availability of the species to determine the properties to take part in chemical reaction and to influence the position of the equilibrium. We are talking about when there are competing species; the equilibrium really not is the actual case when there is a single concentration of the species which is available. There are in fact multiple concentrations in this case and therefore, it is very natural to assume that what plays an important role is the reduced concentration - the effective concentration of the ions which are participating in the reaction.

So, this parameter is also known as the activity of a particular species. It is essentially a factor. Instead of Ci, the concentration of the species, we replace 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 ith term and that is what essentially it is.

The chemical potential which is also the Gibbs free energy of a particular system, let us say it is nu i or delta g or whatever of the ith species. It can be represented as delta g is 0 mui 0 times of R T ln xi times of gamma x.

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 earlier you know earlier derivation etcetera 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 to be some kind of a change in the overall way that the emf is found and in the overall way that delta g is estimated because of this.

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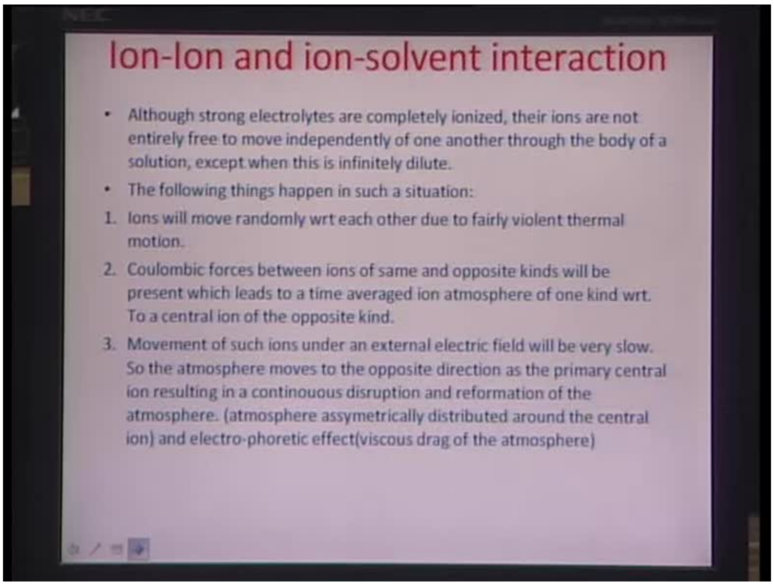

Ion-Ion and ion-solvent interaction

- 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 actually look what happens when you pick the solution with various ions - positive as well as negative. In terms of ion or ion solvent interaction, there are a lot of events which happen once you have such a combination of ions and you have an electric field which is trying to separate these ions.

What are the main mechanisms of movement of ions? One mechanism is the violent thermal motion ions have, almost always so called the 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 motion.

Then there are columbic forces between the ions of same or opposite kinds - opposite kinds attract each other same of course, repel each other, but then there are such columbic forces which would predominate the motion of some kind of ions. and essentially this would The columbic forces between ions of same and opposite kinds will be present which leads to a time averaged ion atmosphere of one kind with respect to the other. Suppose, there is a central ion which is let us say a positive ion and you have a cloud of a negative ions are around it, these would result into a time average defect because forces are continuously happening inside the solution.

Under an electric field, there would be a tendency of this counter ion cloud to go towards the negative electrode because the counter ion is positive in this case and the ion of interest which is the negative ion going towards the positive electrode. In that case, what happens is there is a kind of smearing. 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 they are in fluids, of the different ions with respect to the surrounding.

If we try to model something where we can really get an estimate of what is the participation level of an independent ion, in that case it is a very difficult model. I mean kinematically or dynamically if you are able to investigate, it is one of the great things.

From 1923 onwards, we do have a model and that is exactly what I want to point out here that until 1923, the activity coefficient 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 1923, there was the mechanism which was drawn out in terms of certain set of equations called Debye-Huckel equations and Debye-Huckle theory which should be able to predict the activity using all these different constraints about ion-ion or ion-solvent interactions that I talked about in the last slide.

Let me try and give an idea of how we can predict the activity of an ion mathematically from looking at the dynamics and the kinematics of such reaction.

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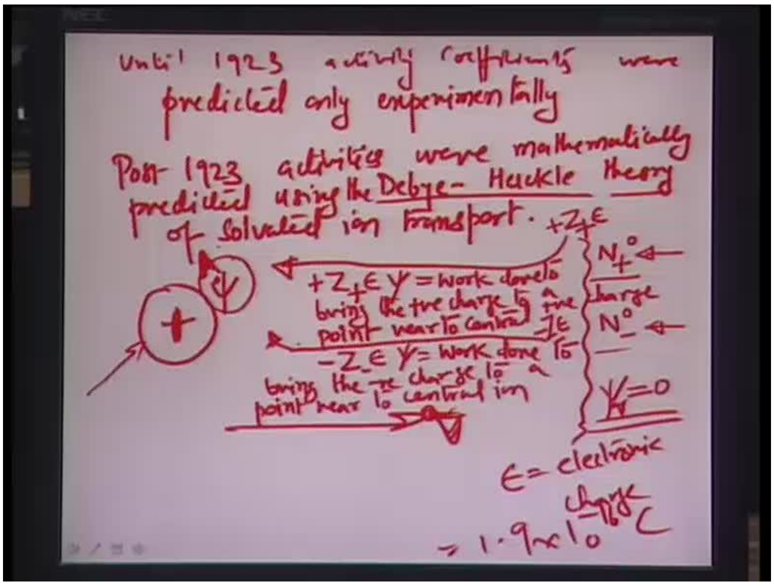

Until 1923 activity coefficients were predicted only experimentally

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

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.

Let us suppose and I am actually going to derive this. Now, I am just going to derive how we can predict the activity. Let us suppose, there is a positive ion here and there is a potential phi somewhere close to this ion. By potential, we mean it is basically field per unit length. So, there is almost always a field times length.

The electric field is nothing, but the gradient of the potential. There is a potential around the central ion which exists and 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 as N plus 0 and N minus 0. We are talking about a ion of interest here as you see in this particular case, there is a potential very close to that ion and there is a distribution of positive and negative ions at a distance infinity from this central ion - central positive ion of interest.

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 the potential phi and as we can safely assume that potential is also inversely related to distance and therefore, at infinity the potential is 0. So, there is no potential due to this ion, positive ion of interest at the distance infinity from it. If I want to bring in some positive charge, let us say with a valency Z plus, what would be the charge? If we assume epsilon to be the electronic charge - 1.9 into 10 to the power of minus 16 coulomb, we are talking about Z plus times of epsilon.

Let us suppose, this is the amount of positive charge and minus z minus epsilon is the amount of negative charge. The amount of work which would be done in order to bring this charge at a point phi would be nothing, but plus z plus epsilon psi. 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 a negative charge near to this point phi the amount of work which would be done is negative z minus epsilon phi. This is the work done to bring the negative charge to a point near to central ion. Of course, you have to do positive work in order to bring the positive charge to the positive center and automatically for the negative charge would come by attraction onto the positive center. Basically, the system will automatically do the work. So, this part is very clear that what happens in the near vicinity of the positive charge.

Now, let us look at what really is going to be the distribution near such a point. Let us call this point A. Let us call this particular point near this, where the phi is the potential as the point A. At A, let us compute what is the charge distribution at infinite distance from this charge.

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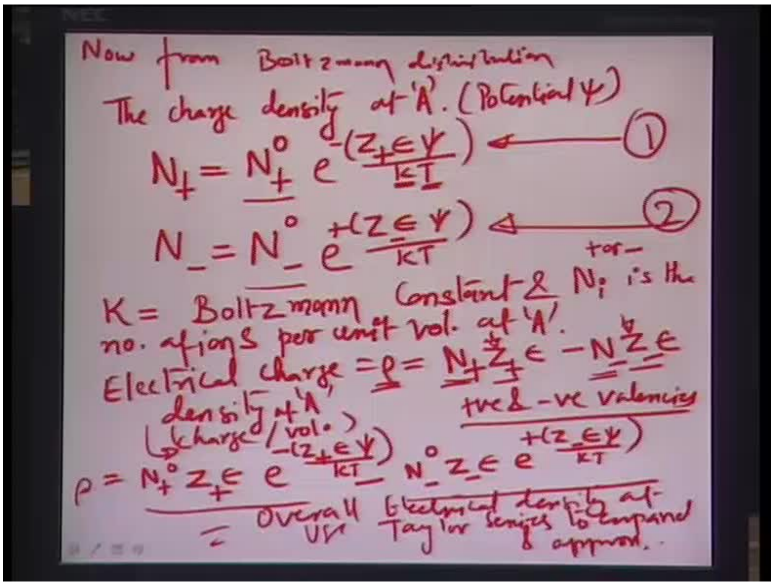

Now from Boltzmann distribution

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

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

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

+or−

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

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

+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 [illegible]

Taylor series to expand & approx.

This is also known as It is also given from the Boltzmann distribution. Without going into the details of what Boltzmann distribution is, I am simply going write that from Boltzmann distribution the charge density at A; remember the point A at which the potential was phi in the last slide. 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 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 at infinity times e to the power of plus z minus epsilon psi by KT. One has to assume that this is a self-driven process; this is a temperature dependent process. If you have a temperature T, it automatically means that there can be relationship between, without doing any external work of course, there is a relationship between the charge density at infinity and the charge density at the point A at which the potential is phi.

Just for the sake of clarity, K is also called the Boltzmann constant and the particular N here let me call it Ni, whether it is positive or negative is the number of ions per unit volume at A.

So, the electrical density at A can be represented as N plus Z plus epsilon minus N minus Z minus epsilon. Remember, Z plus and Z minus are the positive and negative valencies. Why you need valency is because when we are talking about ion transport, there has to be an idea of whether it is a negative ion or a positive ion. What is going to be the total amount of charge - electronic charge that ion contains. Therefore Z plus or Z minus is very important to be included in the equation because they are a function of any ion's oxidation or reduction state. The total charge density that means charge per unit volume This is charge per unit volume rho is given by N plus Z plus epsilon minus N minus Z minus epsilon. From equations here one and two, we can substitute what are the values of N plus and N minus and write the final charge density rho as 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 the final electric charge density as simply a difference between the N plus 0 Z plus epsilon and N minus 0 Z minus epsilon e to the power of minus z plus epsilon phi by KT e to the power of plus Z minus epsilon phi by KT. So, that is the overall electrical density at A. Let us use Taylor series to expand this a little bit and also to approximate it.

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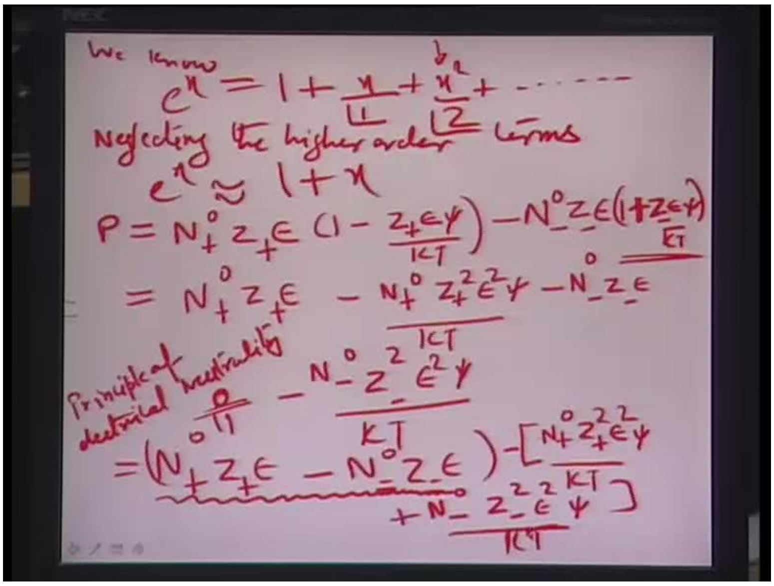

We know

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

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

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

As we know from elementary mathematics that if you use Taylor 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 on and so forth. Neglecting the higher order terms, we are left with an estimation of e to the power x as 1 plus x. If you assume x to be small enough, we can really safely ignore the higher orders. Now, if you look at the equation which we predicted in the earlier expression here, we have this important factor epsilon which is 10 to the power of minus 19 and epsilon by K also is probably going to be in a very small order and therefore, the overall term Z plus epsilon phi by KT is really very small and is insignificant. Therefore, the higher orders of such a term can be safely neglected in the equation.

So, if you put this back into 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 phi by KT. Basically, as a talking the charge density here is given by N plus 0 Z plus epsilon 1 minus Z plus epsilon psi by KT from the Taylor approximation and this is the positive density and negative density is minus N minus 0 Z minus epsilon 1 minus Z minus epsilon phi by KT. That is how you indicate both the plus as well as the minuses. When we are talking about. This is really the overall charge density also which we are investigating. If you 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 plus epsilon minus N plus 0 Z plus square epsilon square phi by KT minus N minus 0 Z minus epsilon plus N minus 0 Z minus square epsilon square psi by KT.

(Refer Slide Time: 40:09) This was actually plus because if you go back here and if you look at what the density is – this is essentially e to the power of z minus epsilon phi by K and this was a little type error here while writing this. This will be 1 plus x - 1 plus Z minus epsilon phi and KT resulting in this sign here to be changing into minus.

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 1 bracket and minus of this whole other term N plus 0 Z plus square epsilon square phi by KT and plus N minus 0 Z minus is due to the space consideration, let us write this term on the bottom here. We are left with the second term here which is give me a minute, plus N minus 0 Z minus square epsilon square phi over KT, bracket closed.

There are several interesting things to be shared here. (Refer Slide Time: 41:45) One is that this particular term which we are talking about here has to be 0 and why that is so is that this is also the principle of electrical neutrality. I just need to explain why that is so? This principle essentially states that if you are talking about the positive and negative charges in a certain solution, there is automatically a chance of these to be redistributed in a manner so that the overall medium is electrically neutral. So, there should be equal number of positive and equal number of negative charges in that extent.

Here when we are talking about the charges at infinity is placed from this point to the central ion which is the positive ion, the total amount of charge that we are talking in terms of... Let us say the valency on the positive charge is Z plus, the valency on the negative charge is Z minus and that distribution of the charges per unit volume at infinity is N plus 0 and N minus 0. The total positive charge that we have at infinity per unit 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 psi is N minus 0 Z minus epsilon. They should be exactly equal and opposite or in other words, the summation of this charge there should be 0 or the medium in general should be electrically neutral.

Therefore, the first term here really is a 0 term. There is absolutely no charge; it is a neutral charge. The second term here is of importance to us because that in a sense is what the charge density really is. Let us actually write it down in the next slide.

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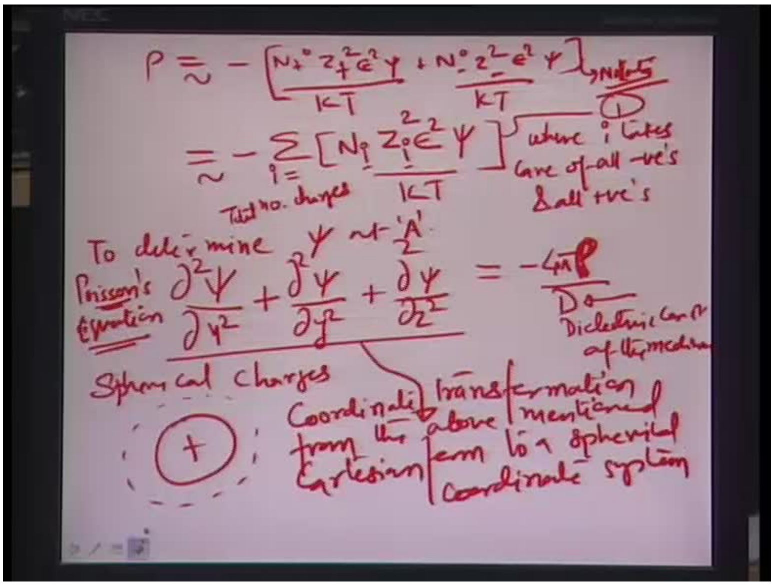

$$\rho \approx -\left[\frac{N_+^0 z_+^2 e^2 \psi}{KT} + \frac{N_-^0 z_-^2 e^2 \psi}{KT}\right] \text{, Notes } ①$$

$$\approx -\sum_{i=}\left[\frac{N_i^0 z_i^2 e^2 \psi}{KT}\right]$$

where i takes care of all -ve's & all +ve's

Total no. charges

To determine ψ at 'A'

Poisson's Equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi\rho}{D}$$

D Dielectric const of the medium

Spherical charges

Coordinate transformation mentioned above from the Cartesian term to a spherical coordinate system

So, the second term, rho effectively becomes minus N plus 0 Z plus square epsilon square phi by KT plus N minus 0 Z minus square epsilon square phi by KT. What is interesting here to be seen is that we can actually notate this in a slightly different way. What I am doing now really not from the stand point algebra, but from the stand point of notation and the idea is that if this notation is continued just for convenience say throughout the equations and we do understand what it means at the end of the day. Then we are very clear about what has to be done.

I would say that this thing is represented by sigma Ni Zi square epsilon square phi by KT where the notation is such that i takes care of all negatives and all positives positive charges in the medium. So, i is something which is the generic subscript. If we were to actually take these ions together and number them as 1, 2, 3, 4 and 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. Therefore, whether it is plus charge density or plus positive valency or whether it is a negative charge density or a negative valency, it can be subscripted by the subscript i as you can see here in this particular equation.

So we are left with the charge density approximately to be sigma Ni Zi square epsilon square phi by KT where i is the total number of charges irrespective of whether it is positive or negative charge.

So all said and done, let us actually call this equation number 1 for the sake of convenience. Let us now look at a little different aspect as to what this electrostatic potential phi would be or How we can calculate the electrostatic potential phi at the point A near to the positive ion. Let us say that we want to determine the phi at A. One way of doing that would be by using the Poisson's equation which gives a spatial relationship of the potential function around a charge with respect to the density of the charge which is available at that particular point. We can write the Poisson's equation and I am really not going into the details of how the Poisson's equation is derived because that is essentially going to be the curriculum for a second year graduate course in mathematics, but we would like to use this equation and try to solve for the potential function for phi in interest of our finding out the overall activity of an ion or ionic species.

So, we have the double partial derivative of phi with respect to x plus the double partial derivative of psi with respect to y plus the double partial derivative of phi with respect to z, the potential function as the phi or the psi and that essentially can be accounted to the overall charge density and the dielectric constant D of the medium. This D is essentially the dielectric constant on the medium - ability of medium also to give way to or to store a charge. This is the dielectric constant of the medium and the Poisson's equation is the relationship between the variation of potential function with respect to all the 3 coordinates and it gives a relationship between that variation and the charge density of an atmosphere of which the phi is to be considered of.

The first thing we would like to do is because we are talking about spherical charges, we would like to transform the coordinates of this particular equation into the spherical coordinates. We are considering spherical charges. If you may remember we were talking about positive charge which is spherical and the atmosphere around this particular charge. So, we would do a coordinate transformation from the above mentioned Cartesian form, this one, to a spherical coordinate system. In order to do that I would just like to illustrate how you would be able to change this, but then it is expected that you basically in one of the homework assignments which I would be giving later on, do and show the derivation. this can be This is available in any of the as I told you before first or second year graduate text books on elementary generic mathematics.

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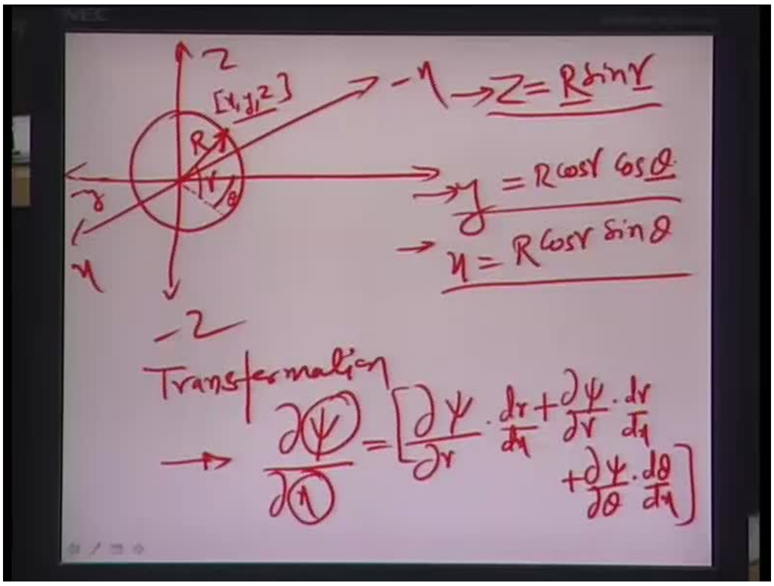

$\rightarrow Z = R \sin \gamma$

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

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

Transformation

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

Let us look at how this coordination transformation would be done. Let us suppose, we have a Cartesian coordinate here x, y, z. This is the x, minus x, this is the y, minus y and this is z minus, z. Now we draw a sphere here, somewhere in center and we assume that there is a radius vector R of this sphere projected in the 3 dimensions from its center which is the geometrical center - x is equal to 0, y is equal to 0 and z is equal to 0.

Let us further assume that we take the projection of this R vector onto the x, y plane. This is the projection of the R vector onto 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. So, automatically this Z value comes out to be equal to R sin gamma. This is 90 minus gamma. So, R sin gamma is the z value.

What happens to the x and y value? Let us further assume that the projection vector of R on the x, y plane is at an angle theta with respect to the y coordinate. In that case, the corresponding y value here corresponding to this radius vector would be equal to R sin gamma cos theta and the x value would be equal to R sin gamma R cos gamma

So essentially this thing is cos ,it also cos. So, R cos gamma cos theta and R cos gamma sin theta. This is what the y and the x values are. This is nothing, but 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 may x when the projection on the y the x y plane and essentially the projection of a projection on the y in the x coordinate.

So, once these 3 vectors are figured out, transforming the coordinates would essentially mean you have to do dphi by dx as dphi by dr times of dr by dx plus dphi by dgamma times of dgamma by dx plus dphi by dtheta times of dtheta by dx. So, essentially this is actually nothing, but total partial differential of phi with respect to x when x is dependent on the various parameters R, gamma and theta.