Advanced Chemical Thermodynamics & Kinetics

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Lecture - 37
Non-ideal solutions, Activity of ions (Debye – Huckel theory) – 2

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Now psi i is here and I have rho i here; let us first do one wave ok. Now what is wave? Wave is basically charge density right.

Now how we calculate charge density? Basically you have to take the density of ions because charge density connected to basically material density and then how the answer carrying charges; as simple as that right. Now when you measure something; something means (Refer Time: 00:41) the concentration ok. So, what we are saying remember this charge density rho i is around a particular cation, say at due to a cation what will be the charge density? Clear, but that is slightly different from your actually number density.

Meaning what I am trying to say is that; suppose there is a ion and it there is a spaces and there is suppose no like attraction between carbon spaces ok; no attractive force, just a very ideal system. Then the density around it will be same everywhere; it would be identical to a bulk density. Moment you are talking about charge is; the density will be influenced clear. Because cations will basically; in fact, vapour around enhance and vice versa right.

Now which means actually, but what you measure; when you add to solution? You always measure the bulk density ok. Because you know the what is the amount of what is the amount of this thing ok. So, what I am saying here is that the density will somehow different; now how do you calculate it? How do you calculate the densities are different meaning what I am saying say here I have some charge here ok.

Assume this charge; I am asking what is the density of molecules of the ions here ok? So, that will be slightly different from the bulk densities, but this difference in population; you can always go back and think in terms of Boltzmann distribution.

How? Because I know that if there is some stabilization ok; compared with the bulk densities ok; I have some preferential accumulation I have just simple as simple as that. Now, what is this energetic thing is coming from? This because of this potential variance if I put a charge here the charge will gain an extra energy due to this potential. That will (Refer Time: 02:41) an energy difference and that will be basically controlled as a Boltzmann distribution.

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So, what I am saying mathematically is I have a charge density; which I am writing as c; not charge density is there, this is basically the number density or say spaces i. So, this is (Refer Time: 03:03) algorithm. And then I have (Refer Time: 03:06) j ok; in the sense that this was i and this is suppose j; i and j can be equal; then in case cation cation it can be cation anion.

If it is cation and cation; you can think that there is a repulsion right. So, the density here will be less than the bulk density, other if it is a cation anion, the density here should be more than the bulk density; that is a simple concept ok; j can be cation i also can be cation ion. What I am condition here this thing c j, which is basically the concentration of the spaces j and some distance from that central thing which is has a spaces i ok; this ratios meaning which is the bulk ratio, will be proportional to the Boltzmann factor ok. Then what is Boltzmann factor; then what is Boltzmann factor (Refer Time: 04:01)? Which is basically e to the power minus some energy capable right.

What is this energy? This energy is having because I put a charge j at a this some distance ok; from the central ion which is i, but distance I do not need to know because I already know due to this charge, the potential created this phi i clear ok. So, if there is a potential created phi i and what is the charge on the z; sorry on the j? Charge is basically like; it will be z j suppose present to be I will say z i was for i; z j is for j I have to always multiply by fundamental charge.

This is basically Q times the potential; potential due to i, this is the energy if I dividing by k B T; then I get the Boltzmann factor ok. This can be repulsive variant ok; it charges an of similar kind or can be attractive clear? That is having what is a sign now relating sign of this phi and j right. So, this thing will control the ratio ok? Now actually I do not mean by number density, I actually mean the charge density. But I can always write the number density first and then derive the charge density; how? Because I know what is the number density of; sorry charge density around this cation rho i ok.

So, this is basically the density of the cations and density of the ions together; meaning I am writing as something like around it ok. So, I just slightly surround around it basically some cations and anions are accumulate ok. Now what is the concentration of cation like and anion c plus ok; what is the charge of the cation which is z plus ok. And then remember; this is actually this density is what writing in terms of morale mole sorry of for 1 mole ok. In the sense write I can actually write what is the total charge here; c plus let me just I think can I have alternative definition; just a minute.

So, what I am writing is basically the charge density ok; charge density is basically number density multiplied by charge as simple as them ok. Now this charge density for a kind of mole density (Refer Time: 06:45); for cations I have z plus cation; each cation is giving you how much charge? Let us say z plus into e is minus c basically, but then for 1 mole; I have to again multiply by e times; halogen number clear? That I can directly replace by F; that is a fundamental definition of this charge Fahrenheit right and this is (Refer Time: 07:12); Fahrenheit kilo model ok. Similarly for the anions also I can write it as c minus z minus into F clear ok.

Now, let me one thing; so these things c plus and c minus are ignore them, but I can always use these equation; I always know what is the cations overall density and the anions overall density number density ok. Suppose I gave you sodium chloride; you dissolving into some (Refer Time: 07:44) whatever, what do you know? How many number of sodium atoms sodium anions are there per unit volume right, but that is drastically modified in presence of the other 2 atoms or other sodiums; that is the thing how it is modified because of this realtion.

All I know is c j 0 something those things what I am saying here is the this c plus is nothing, but c plus 0 times a Boltzmann factor ok; which is nothing, but e to the power minus, I am talking about now j is being plus. So, I will write plus z plus e phi i by k B T clear? Into there was an F clear. And then I have c minus c minus I can write the c minus also the same as c minus 0 times; e to the power minus z minus e phi i divided by k B T clear; so, this is the charge density clear.

So, how do you get the charge density? Charge density is basically the number density multiplied by the charge density ok; for charge. But that thing I cannot measure actually c plus c minus because that will be modify right, but I know always that is a connection with the bulk density which I have. Because I know how much amount of the ions is dissolve ok; for that cations, for the anions; for example, if I need sodium sulphate Na SO4; the concentration of the bulk concentration of the cations should be twice than anions clear ok.

But anion know a bulk concentration, but that charge density it is not connected by the bulk concentration; it is connected by the local concentration ok. How local concentration is defining? That is basically the local potential how this change; clear? Due to the centre ion, now i is centracting with i same and you may cation is centracting cation, cation is centracting canion; all these things we have to concentrate clear. For then I (Refer Time: 10:02) expression for the charge density ok; now this is still not a very very bad expression; in the sense that it has e to the power i phi all these things.

Now, the thing is that what I have is cavity and this first thing you do is basically expand the exponential. And do not consider the high order terms ok; e to the power x I can write it as 1 plus x; in this case it is written by minus x. So, I just take 1 minus x I am say you what is happening; what is just do it, I have basically c plus 0; there is a F here yeah any question?

Student: So, here z plus z minus (Refer Time: 10:39).

Which one?

Student: In the second step.

Here?

Student: (Refer Time: 10:45).

Ok.

Student: I will be multiplied by z plus.

Sorry here is a z plus also; yeah there is a z plus there is a z minus also yeah. So, I have c 0 plus z plus F into let us expand this thing expand if I during it will be 1 minus x right; x is what? z plus e phi i divided by k b T ok; I will have a similar term for the minus let us assume it. So, I have c can you see I have c minus 0; z minus F 1 minus of all the classes will be replace by minus by k B T clear.

It was very complicated ok; let us see how it is going alright. So, when it is write it this term and this term; let us first write you know what is that things c plus 0 z plus there was e sorry not e; E and a combination of (Refer Time: 12:07) And then I have c minus 0 and z minus F; this is basically addition of this term and that term one terms ok.

What is this? What is c plus? 0; c plus 0 is a bulk concentration of the cations, you can think how many numbers are there per uniform ok; z plus is the charge, F is common right; c plus 0 into z plus and c additional c minus 0 into z minus has to be 0. Because the entire thing is electrically neutral right sodium sulphate charge is plus 1, amount is twice than the sulphate. The sulphate charge is minus 2 amount is just half, if you just add it this first you can such as 0 clear ok.

Then I will be left with only the last 2 terms; last 1 is second term and the fourth term ok. First and third addition is 0 because of electrical neutral; here they have the entire thing again it is a entire thing because actually it is a bulk concentration which makes sense. C plus and z plus locally may not cancel each other with c minus and z plus ok; there can be x term that is the meaning of the ionic atmosphere clear.

But in a bulk sense of course, they should always cancel each other this is basically concentration times the charge of kind of concentrations which on the anion change has to cancel clear ok. So, the first 2 terms got cancels; so, what I will be left with is plus is this 0 for electrical neutrally ok.

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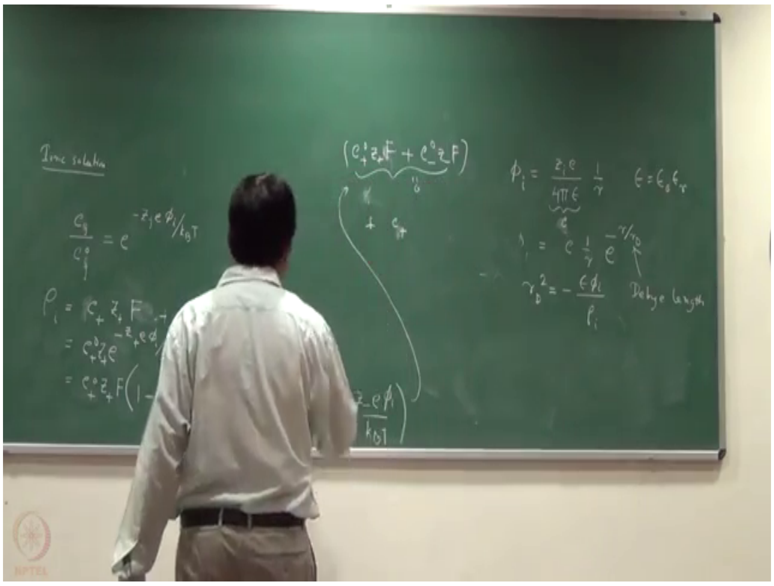

And what I have been having is basically let us see I will have let us look at here, I have c plus, I have z plus; z plus will come twice. So, I have basically z n square kind of thing right. So, I have here c i call let me just as plus the first write it as plus.

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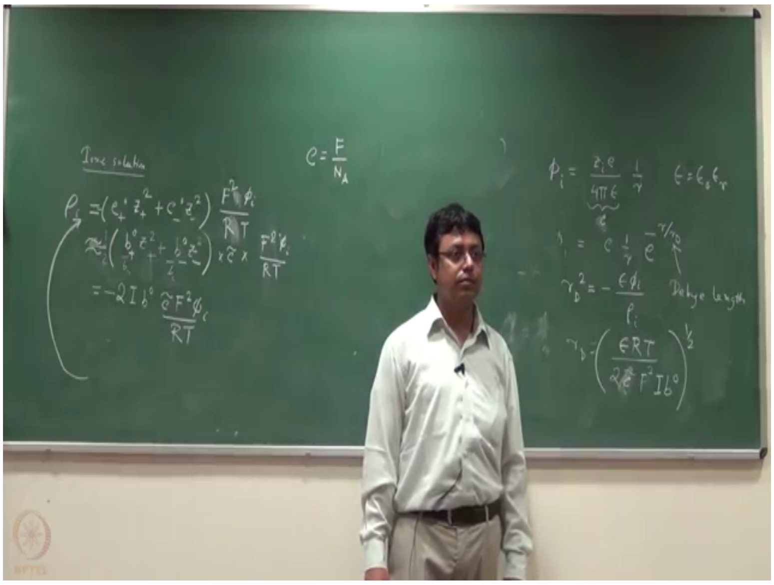

The first term got cancel then I have c plus 0 rightly between these 2 terms what is the difference? C plus z plus these are the different term F and other things are common ok. So, I have c this thing c minus 0 z minus square what are the other things I have got F l; e phi i by k b T clear F e phi i by k B T clear.

Now, the thing is that this I can also modify like at this stage in the sense that what is e? I can write let this ok. So, then these factor will be if I replace e by F by N A; this will be F square phi i, N A into k B will be R. So, I just write F square phi i RT ok; now look at this term what I am going to prove is basically the ionic strength ok. The ionic strength what was the definition? Remember it was basically what I tell me what is the definition? Half you just wrote it right.

Student: Summation.

It was a summation right.

Student: 0 yes.

But in the summation; if you remember there was basically molarity right, but this is basically bulk concentration means this is a molarity ok. Now we have to make another approximation in the sense this molality and molarity; there is not much difference ok. So, if we maintain approximation ok. So, what I am saying here is that we can actually write it as something like again this is one approximation ok. This term we will write it as something like b plus for the bulk molarity ok; z plus square plus b minus z minus square into basically I have to multiply by the solvent concentration, but what do you mean by this? So, what is molarity anyone definition molarity.

So, this is basically number of moles of solid per gram of the solid right when you define molarity; it was basically number of moles per?

Student: Mole neutral.

Litre right; so there should be a connection between solvents amount to solvents litre; that is basically solvents molarity; that will automatically come. Just from molality to molarity what I convert. I have to actually write also like say 1 kg of water means how much in terms of the ohm right; that is why this concentration of what i is call clear that is the dimensional thing ok. And then I will have basically all this other thing which is F square phi i by RT or this already I define as ionic strength, but there was a half factor ok.

So, this will be nothing, but twice the ionic strength, but remember it ionic strength definition I was writing z x square b plus and there was divided by b 0; that was basically the dimensionless thing just a unit ok. So, what I will be having here is this rho i which is the charge density ok; for the ion spaces which is equal to twice I, I should have b 0 to specified divide by b 0.

Then only get I and then I multiplied by 2 divided by half; I mean I am multiplying by half that half; this b 0 thing was the ion strength right. That is why I am multiply by 2 and b 0 and then the rest is ionic strength times I have the solvent concentration F square phi i by RT fine I am basically reducing the problem alright.

So, what I got is basically rho i is this and then rho i is the rho i yeah; then what is what will be the mole r D that is the straightforward thing. So, I have basically rho i here that is the rho i thing ok. So, this r D square clear ok; so, what are we having is just a minute. In the rho i definition; if you remember that we took a sum right it was 1 minus x; (Refer Time: 19:58) minus sign here because I was taking the summation of these thing ok. So, there will be a minus sign here minus sign here minus sign here that minus that minus will be give a plus basically.

And now I have definition for r D; so, r D if i just write it this will be epsilon RT divided by twice rho; rho is the charge density 2 c tilde F square I b 0; whatever (Refer Time: 20:30) I have something ok. Now look at it now this D value after utilize the rho i as a very interesting description the reason is there was a phi i here; the phi i is got cancelled. And then everything you can calculate you know the permittivity; so, bulk thing it is a R it is a T Q concentration of the solvent, Faraday constant, ionic strength which you can calculate and the unit term molarity fantastic.

Now, actually I can calculate the potential because I know what is happening clear; from everything which you know fine r D is known, but at the very beginning what I said is the, I have to calculate what? I have to calculate the work done, it was basically l n comma plus minus was the work done divided by this thing ok. Now that is the only part left, how it calculate the work ok? If I can do it, I can get a (Refer Time: 21:37) all the divided by conclude ok.

Everybody is following at this point right alright, but you now you can read at least and you will realize because that many things here. Now just go a step and just think ok; so, basically what I am saying here is that; I have to just calculate not a (Refer Time: 21:58) activity coefficient ok. And the activity coefficient already I wrote that this is the work done was equal to the mu's, addition of mu's right at the very beginning I get and wrote it basically it is work done divided by s RT that formula ok.

Now, what is the work done? That is your trigal work right; electrical work; I have to calculate electrical work done everybody knows like; if I know the potential if I doing a charge right it is a basically charge into potential; I am just going to derive that ok. For that potential and for any arbitrary charge which is like say the ith charge which is at the centre clear and later on try to derive the work of charging ok.

So, it is something like think about it like; there was a ionic atmosphere right and centrally there is a charge setting there ok. All I am asking is that if I charge and discharge this central it is a electrical work ok. If it had charge and if it did not have charge what will be the difference? There will be an difference in electro statistics and then if I just multiply by the charge and I should get the work done ok.

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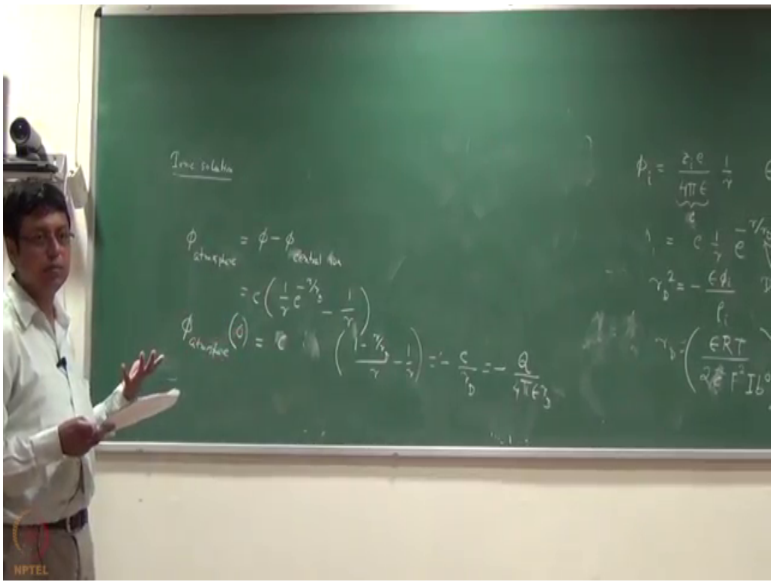

Which means actually this potential, but everything when you calculate the work done all I need to know it is a potential because, potential is by definition is the work done due to the unit positive case charge right; if I multiplied by the charge and get the work done, as simple as that.

Now what is the potential I am talking about? This is basically the potential of the atmosphere. So far what I was writing phi i is the potential due to the charge; now I am asking what is the potential due to its atmosphere on this charge because it is a back action right. Now, if I want to calculate it is basically the total potential minus the potential which this guy is creating.

Thus basically the central ion ok; now let us think about it what is this phi? Already you know like mathematical expression for phi for the ionic atmosphere; it was not exactly 1 by i; it was 1 by i times the e to the power thing just; let us write it. So, I have some constant c and I had one what was that basically 1 by r; e to the power minus r by r D right and minus the central ion will always have of 1 by r i;.

Because it is a charge that is what I was telling right; this is for the charge, this for the ionic atmosphere ok; the difference will be basically the net potential which got I am clear ok. So, there are kind of 2 potentials here, one is due to the charge and one due to its atmosphere which is also composed of mini charges. But those charges were moving and create a continues distribution in a atmosphere clear ok.

Now if I do it ok; so whatever we want to calculate this atmospheres like effect at basically my central location because that is the important thing where actually we ion is sitting; which means actually I want to calculate this phi atmosphere at the 0 location. Because potential is varying and again now a picture in mind I had a central ion surrounding it; any of this central ion is very alternate I can chose a cation, I can chose a anion whatever ok.

But surround the central ion always I have a diffused cloud, everybody seeing a diffused cloud something like that ok. But everybody that everybody concept is basically that is a vocalized judge point judge and all others are actually just kind of giving you an average field, of that average field and an excess charge that is why there was a charge density clear ok.

So, that is what we calculate, now the question is close to 0, which is basically close to the origin what will be I will be basically take this expression, take the limit of this expression one basically this r ok; when this write (Refer Time: 26:38). So, just let because write it and then I will just (Refer Time: 26:50) display it yeah 1 minus (Refer Time: 26:58) how do define the potential.

Like what is the charge like located on it say basically what I am saying here is that I am talking about an difference in the ionic atmosphere ok. When I am close to the origin; now remember what is that definition basically of having like; what is the definition of the work done electrical work done. So, you basically bring and unit positive distance from infinite distance; to this distance, which means what I am trying to say here is that ok; when this thing like the divided will be very very large ok.

There only this will be valid why? Think about in your different way ok; different way of thinking in the sense like, if I have a very local atmosphere ion and anion; you will have very discrete cations and anions.

But if you want a diffuse of description you have to really make it large ok. So, in the sense like only this limit or like why this r D is basically much larger; then only I can make this approximation which means 1 x is actually small which means I can just write it in a very simple role clear. So, there will be 1 minus x I have just not writing this thing you understood right.

And then I am writing it 1 by r 1 by r will be cancel and basically the left with something like minus mu constant times divided by basically r D; there was 1 by r clear constant divided by r D right. So, that is basically (Refer Time: 28:58) the atmosphere; how it is basically creating at the centre position at basically r D equal to 0 position close to that.

Now the thing is after this is very like compact thing what was c? C was basically this entire constant ok. Now what is z into e? z it will I said it is a charge density right; write an this write the constant as minus Q divided by 1 over 4 pi epsilon into r D something like that. I am just using slightly different notation here ok; now what will be the work done? Again work done is basically this potential times the charge.

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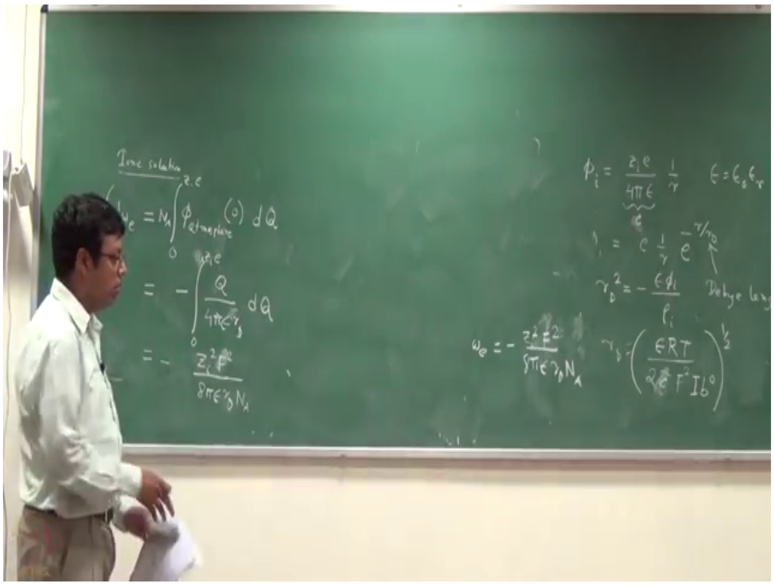

So, when m is done; so usually you say that ok; so, I will find the work done I process write first the differential electrical work done ok. And that I will say that it is basically that potential which is the atmosphere is giving and then suppose I am bringing give you amount of charge.

So, I have basically a defective potential which is the difference between the potential created by the ion and the atmosphere ok. And that potential we calculated at the origin which is my centre; now I am saying is that the work done if I actually add little bit charge to that effective potential; will be basically charge multiplied by a potential ok. Now basically (Refer Time: 30:40) divided and integrate it from where?

I know that the work done will be; basically it is work done due to something called charging. I did not have something there ok; now I am basically adding charges how much charge I can add? What is nothing, but z times a. So, this will be basically the work done; i add 0 charge and then I am going to up charge fractional charge, I am included it ok.

And I am actually making up 2 the cation charge of the anion charge; that will be decided by whether it is z plus z minus clear; that is the differential work done. And then this will be the integrated work done clear ok; now this is basically the work done for 1 cation. If I just ask you what is the molar thing I have to of course, multiplied by (Refer Time: 31:42) number because this is for 1 charge or as you can see N A into e again what will be give you an F ok.

Now what ultimately we will get is what we have minus Q 4 pi epsilon r D which is write it here; half minus Q 4 pi epsilon r D, d Q that integrated into the 0 and any z i into e. Now again what is so; you can see here right, it will be basically Q square, it is a step or integration ok.

Now that Q square I will again write that as z into e and then which means I had here as you can see that the Q square will have basically z 1 square e square kind of capita clear; I am just skipping the step. So, I will eventually have and this N A into e I can always write as F right. So, eventually have something like z i square I had F square while the F square is coming, it will be basically everything square right.

N a square e square is basically F square and then I have 8 pi by 8 because it is Q square by to integration ok. I will have 8 pi epsilon and then I will have r D, but just 1 minute just 1 minute I will give you one charge you know ok; I just did a mistake sorry d work done at the (Refer Time: 33:43); then this why?

Because this is for N a I can have x square basically it is work done due to one charge and then that will be square or (Refer Time: 33:54) multiplied by number; I cannot again a square ok. If I do that think about it; it should be Q square, Q square will be basically z i square e square. So, z square e square by 8 pi epsilon r D ok; there is a minus sign and then there was a N A then N A square F square I can write as F square and then I have to divide by N A clear.

So, I am level done and by it is a (Refer Time: 34:31); this is basically the work done ok. Now I am actually done with the everything, I have actually work done definition in the work done definition I have an r D; r D also I know ok. I am totally done, all I am doing right now is to go back to my original definition and write the numerical thing; which we wrote at a very beginning ok. Let me also write this thing directly this is basically minus z i square F square divided by 8 and epsilon r D N fine this is basically electrical work done for 1 clear ok.

Fine; now final thing so where I have is basically l n gamma plus minus right that is what we wrote. What we wrote that time? (Refer Time: 35:42); we wrote basically it is work done divided by s RT right; now the work done is for cation is for anion at basically at a total work done ok.

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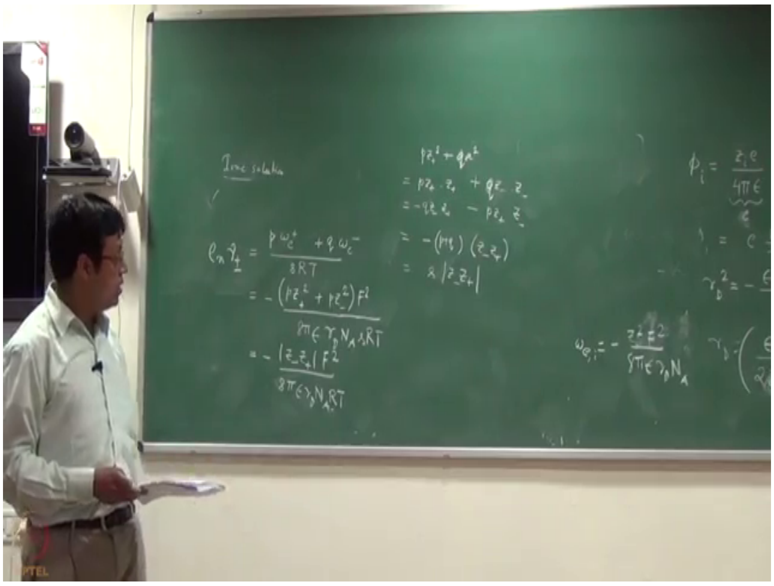

So, I have to basically it is not actually w by e s, but w has 2 parts which is basically electrical work done for the cation plus electrical work done for the anion. Because as you can see what we derived this for i electrical work done for i; it is z i square F square right. So, i have to add the cations work done anions work done because there are many ions, there are many central thing which was the particular ion. This thing and then how many cations are there?

Student : Q.

Q or p equal I think; it will p right how many anions are there? Q divided by s RT s is basically p plus q done ok. Just use the formula what am I derived ok. So, for anion minus sign here and then what I have is p z i square ok; we just write it. For e plus I will have write z plus which z plus square plus p z minus square divided by I will have x square just write together minus F square. And then what I have? 8 pi say epsilon r D into N A ok. Now think about it, in the original expression which divide the like I am trying to go back actually; I am trying to match it the original expression there was z plus z minus modulus remember.

Ionic strength times z plus z minus, but here I have actually z plus square z minus square, but I can always play tricks how? Think about it this p z plus square plus p z minus square just look at it; p z plus into z plus right. And this is p z minus sorry q z minus into z minus. Now for electrical neutrality we already said p z plus has to be basically minus q into z minus; right has to be. So, that thing I can write it has minus q into z minus z plus. And this (Refer Time: 38:27) I am writing into minus p into z plus z minus. So, I write actually z minus z plus thing and this p and q is basically s right; now basically this s will cancel clear ok.

So what I got is something like I will just write it here. So, I can write it as minus p plus q z minus z plus, but z minus z plus if I adding in terms of modulus, then is minus sign will be inserted because z minus itself is, if I add it say sodium sulphate; I shall write minus 2 ok. So, which means this is nothing, but s; the negative thing is already included of modulus of z minus z plus or z plus z minus whichever you have will have ok; now let us bring it here.

So, basically I have minus s and s where is the s RT there was a s RT ok. So, I have basically z minus z plus modulus F square divided by 8 pi epsilon r D N A RT clear. Let me just check whether I have written correctly z plus z minus F square 8 pi epsilon tau d sorry r D RT fantastic ok. Now, what is r D? r D is this big value it is actually write it.

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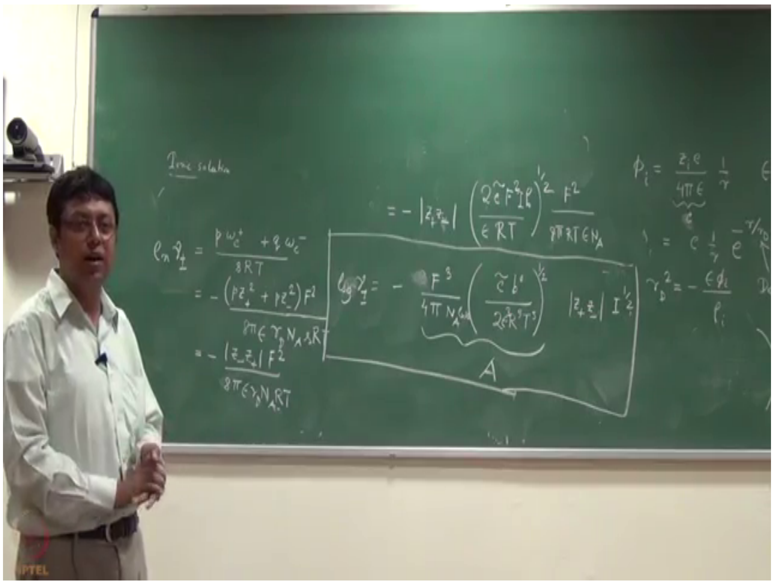

So, minus is basically 1 upon r D; I have to write this thing ok. So, I have to write it in terms of the reciprocal ok. So, and minus z plus z minus modulus and what I had basically epsilon RT right; I am just writing epsilon RT ok. And what I have twice e F square i into p 0 right twice e F square i into b 0 ok; that to the power half that is basically 1 upon r D ok.

And I have rest of the thing which is basically F square and then what I did 8 pi RT and then I have epsilon N a done 1 over r D I already wrote ok. So, I am just rearrange it; it is basically minus, just a minute if I am writing in terms of r square (Refer Time: 42:00) ok.

So, there is a F square here right I can actually take it out it will be F cube ok. So, I will have basically here F cube divided by, as you see we can simplify where you get just one minute I think it is right, but we can test the (Refer Time: 42:38) just 1 minute yeah. So, I am basically trying to just write it down the final expression will have to (Refer Time: 42:50) between. So, these 2 think about it if I write 4 pi here insert 1 2 here; this becomes 4.

So, this 2 and this 2 gets cancelled. So, I am basically have first write the outside thing 4 pi N A inside thing that 2 inside ok. So, I will have 2 in the denominator I had RT here let me insert it. So, then I will have R cube T cube right and then I have an epsilon here and did I miss some epsilon? There is a epsilon here. So, epsilon also if I insert it will be epsilon cube R cube T cube I have let me just write epsilon first epsilon cube R cube, T cube ok. And what I will have in the numerator? I will have basically c tilde in Adkins; he has written it as rho the problem is that rho is using as charge density as well as this was (Refer Time: 43:53).

So, I assuming as c tilde, and then what else I have? F cube already I have take out, I have b 0 ok. And then I am just writ it; I have I to the power half here that basically the half; I have z plus z minus I to the power half, this was basically the A; A plus A minus I did not; have done; so this is the numerical theory ok. Now let me just quickly review a summary ok; how to do it. So, now, look at the thing here the thing here is that everything in the cabulate everything, all are bulk properties ok.

These are constants; epsilon RT concentration sorry molarity of solvent b 0 is the single testing, z plus z minus is just the charges, I is the ionic strength. So, that actually now you can calculate, some textbook actually write it as I mean I think initially it write it as log gamma plus minus which means actually there will be a ln 10 factor because they wrote it as log. So, this is basically the given in the (Refer Time: 45:15) law and it is it was basically first analytical expression for how the ionic like how I can actually calculate ok.

The activity for ions again let me actually just give you one quick summary what we did ok; first in first we said that there was a solvent how many hours are left away? So, first in first there was a solute 2 hour class right yeah. So, we said that for the solute I can use Henry's law ok; which is basically looking at that component which is less amount; x b tends to 0 that limit actually Henry's law is valid.

It is a ideal behaviour, but not only it is ideal; it is an ideal dilute behaviour. So, it is no ideal dilute solution, but then it is said that how value is the dilute. We said that we even for ionic solution even one 1 mole fraction is too much ok; we can only use 10 to the power minus 3 millimolar or less where it shows a like ideal behaviour. So, the departure is more for ions which means the ionic activities are much more non ideal in nature, clear ok.

Now the question is why ionic activity? Because the now we have to consider the specific interactions between ions ok. Then we asked the very simple question fine then let us actually go back and think about what is the ionic activity ok? And the ionic activity will be something there is a total activity minus the ideal activity and that difference will be basically the non angle thing.

That non angle thing I can always say that is the Gibbs free energy difference and that Gibbs free energy difference has to be connected to the work done; which work done? Which is a non p v electrical work done clear ok. Now we wanted to calculate the electrical work done; electrical work done how do you do? You basically need to know the potential at some point ok. And then due to the charge there is some that due to the charging basically Adkins has written it as a work done due to charging.

As if there was nothing and then you are putting basically a (Refer Time: 47:32) z i charge there and that work I have to do. I can think that I have 1 z i here, another z i here there 1in of this thing. So, finally, I am to take a sum over the work done due to cations multiplied by the number of cations, work done due to anions multiplied by the number of anions fine that we did actually in the last step right. And then this is a side coming from just the mu thing but then a question is if I actually giving you a something in the back thought because if I just traced back in the reverse way ok; there was a work done.

Now then, how to calculate a work done? Then I need to know the potential as simple as that; what potential? Now there is a interesting thing now we have to module a system ok; it is basically a distribution of charges ok; ions are moving around. Now there are 2 things moving around is good because if I consider one ion, other ions are moving so fast I can think it as a continuous distribution then I can actually bringing the concept of density ok.

So, there is a ionic atmosphere which has some density and there is a ion setting here; the ion is causing a potential which is clearly to warning, by the dense thing which is the ionic atmosphere which is a continuous charge distribution that has basically and 1 over r times e to the power minus r time distribution ok. But anything by e to the power minus r should have been defined which are characteristic length any decay. Like it is a decay constant you can think with respect to a like length decay right now we have to calculate it. Now the interesting thing is that this potential difference ultimately you will be multiplied by charges and that is how calculate the work done this was the step which is just before.

Now, the question is how do you calculate the potential? Now we use Poisson distribution. Poisson distribution we can use only when there is the continuous distribution on charge not a discrete distribution. So, it is a there is a discrete charge around it there is a continuous distribution and then we will sum up for all the discrete charges. That discrete charge for example, some discharge for a different charge; now it is beyond the continuous distribution because when you are sitting over here, this guy is moving actually that is getting a continuous charge distribution ok.

So, that is the trick that play how do you get it? Now we use the Poisson's distribution ok; use thus idea of spherical symmetry ok. So, it is equation would be only the radial distribution; radial part of the radial distribution function. And then basically you calculated what is the derivative of the like potential ok; which will be connected to the charge density ok. Now once I say this is connected charge density; I was also had to calculate the charge density; how do you calculate the charge density? I know the bulk number density.

But the local charge density will be modified due the presence of a particular charge which we are looking at where ultimately we will average; so, for all the charges; now these local charge how it is changing? It will basically shift the energy levels up or down depending on whether this is same charge or different charge; which means there is a kind of Boltzmann factor ok; like n by n 0 there is a energy level difference how do we calculate it?

I can actually calculate the energy which is due this charge how much is the energy which is basically the potential due to this charge multiplied by the other charge z j whatever will be ok. And that will cleverly calculated the charge density by saying the charge density is basically the number density; times the charges. There was an exponential factor, but we basically truncate to it, why? Because these energy differences will be small compared to the thermal energy k BT, then we truncated it and we got the basically the charge density factor that charge density is connected; since it is a continuous distribution of charge density is connected to the potential through Poisson's equation. And since, the potential had this characteristic length having expression for RT d by length ok.

This is the back thought basically; probably they thought it in this way alright I will stop here.