Advanced Chemical Thermodynamics & Kinetics
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Lecture – 39
Electrochemistry: Insights into Electrode Processes, Ionic Conductivity – Part 02

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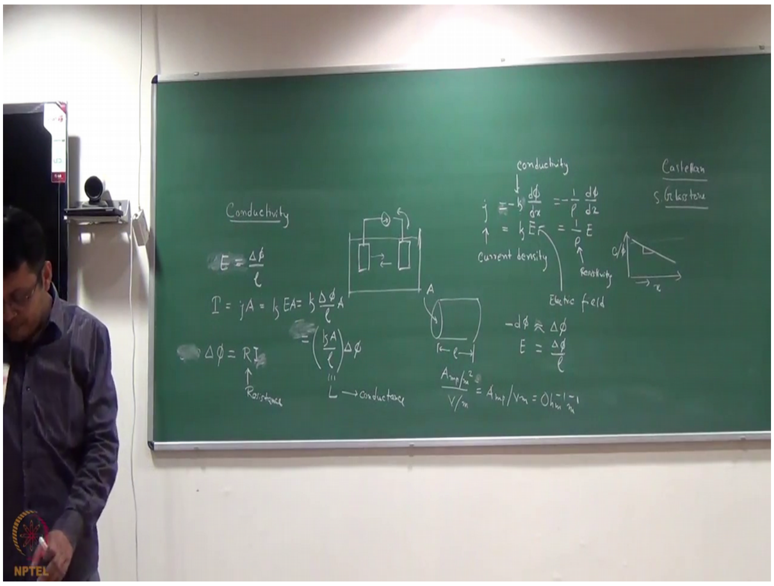

So we just talk about conductivity today. Now, when we talk about conductivity and when we talk about electrode concept like I have 2 electrodes and these are connected and this is solution, let us say and we actually what we said that there are many conditions that affect it. One is of course, like how the electrons are flowing? Right, but more important is basically how the ions are flowing.

Now, there is a big difference, we first give you a quick review of the electron thing, which you already know like Ohms law and everything, but then why ions are different? Because ions are actually mass dependent, different ions can have different masses. So like cation can move slowly than the anion and vice versa ok.

So, what will happen due to this movement? That we are going to basically formulate and how the basically the conductance of a cell will be dependent on that, we will actually define, what is conductance. Now, for I am just using for this portion ok, you can just read the Castellan book there is one beautiful discussion here, you can also read Harkins ok, but Harkins I think the discussion is very brief, very brief ok, alright.

The best discussion for this chapter is in Glasstone book, it is a very old book Samuel Glasstone and either it is physical chemistry or this electrochemistry book also by Glasstone, but again the notations are different in Glasstone al right.

So, the first in first, let us define a quantity, which is known as current density ok. Now, there are different forms of Ohms law, what we studied is basically the current like the potential drop, it is proportional to the i current is proportional to the potential drop and then the proportionality constant is the resistance ok, but here just took as slightly different, but this is also Ohms law and basically it is a that is the current density is proportional to a gradient ok.

Now, the question is suppose, think about a very simple thing let us say, diffusion we will talk about it ok. Now diffusion will happen, diffusion is what? It is basically, migration of masses right. Now mass will move from one side to another side, if there is a concentration gradient ok. So, we will always talk about something some quantity, which has a gradient in space. So, that you can take as x or z whatever some point like suppose the concentration, if we have a flat profile in the concentration, there will be no net flow of mass ok, but if we have the concentration is changing like this ok, then only we will have a flow right.

Second thing, if you think about it this mass actually, moved in this direction a (Refer Time: 03:42) concentration to low concentration ok; however, the gradient which means has to be necessarily the slope, how this is changing? Right that is negative here ok. So, we will talk about it, when we will discuss diffusion. So, similar thing is also here ok. Now current density means, how many electrons are flowing per unit time, per unit area?

Now, that will be proportional to a potential gradient ok, you know that any current flow actually happens, because of potential gradient ok. Now potential gradient is I can have del phi del x, but if it is an one dimensional current i can write d phi d x and then there will be some constant, if I just write ok. Now the question is, if I write it in the d phi d x way think about it? When I am going in the positive direction ok, if this is the positive direction I actually have a negative slope. So, d phi d x is basically negative ok.

So, this can be concentration, this can be potential if this is concentration, it allow diffusion, if this is potential we are talking about now electrical current flow right. Charge flow means current. Now the question is to make it consistent ok, we always use a minus sign. So, that minus d phi d x is positive and the proportionality constant in this case, we called as Kappa, Kappa is known as conductivity right.

So, this is nothing, but conductivity right and already you know that what is the negative gradient of potential? Um is electric field is by definition ok. So, electric field is negative gradient of potential. So, this is nothing, but kappa into E ok. So it is basically, electric field right.

Now, this is actually Ohms law in a different way ok, but then we can actually, write it like this say for example, if we write j is the current density ok. Now usually, we write Ohms law in terms of electrical current right. So, current density means actually how many, how much charge is flowing per unit area per unit time. I just recap current means actually per how many charge, how much charge is flowing per unit time Right, so I have to just multiply by the area.

So, which means suppose if I have a conductor ok, which has some cross sectional area, let us say A and the length is something like say l then I can actually write this d phi d x this d phi ok. I can approximate that this is not a differential change, but this is something like say, delta phi ok, which is delta phi. Delta phi is basically the potential difference between these 2 points ok.

And then I can also approximate that this E ok, will be basically gradient of the potential negative gradient of the potential ok. I am writing it just 1 minute basically, that is minus d phi as delta phi I can always choose that and then the E is nothing but delta phi by l ok, this is just gradient ok, but again I am basically switching from differential notation to a finite notation, but this is valid if the like gradient is uniform all right.

Now, what will be then my current, what is I? Let me first write the delta phi ok. So, delta phi is nothing but I have, I wrote it as E as delta phi. E is basically, delta phi by l right and then how I define the current I with current density?

Student: j.

So, j times.

Student: A.

A right. So, what is j? j is basically my kappa into minus delta phi d phi d x. So, I can write it as kappa and minus delta phi delta is I can actually write as E right. So, this is actually familiar to you ok and then I can further, write basically kappa instead of E, I can write it as delta phi by l ok.

Now, you see that what I have? I have basically kappa, I am missing 1 A, now this entire thing kappa A l, that is basically a constant because, kappa is the proportionality constant of the current density ok. If A is fixed, l is fixed that is also a constant that is what, how you studied mostly the, this form that if I have a potential difference delta phi ok. The statement says basically, the current flowing is proportional to the potential difference right, I is basically proportional to this thing ok.

Now when you write it you always write it as delta phi or some textbook like b 2 minus b 1 or b a minus b whatever and then I can write I into R the proportionality constant is a resistance. So, whatever we have actually is inverse of resistance right, which is known as conductance ok. So, this I am just writing as conductance or I could have actually written this equation as delta phi is R into I, where r is basically the inverse if conductance, which is resistance clear ok.

So, just and then how can I actually discuss the units in a just (Refer Time: 10:27) notation and mu I wrote as (Refer Time: 10:31). Automatically here just like, we wrote as conductivity, you could have actually defined inverse of conductivity ok, it is known as resistivity ok. So, you could have just written as 1 over rho d phi something like that fine, this is basically resistivity ok.

Units I will start from here, so I everybody knows right SI unit is the ampere ok, charge per unit time right. Now, what will be the what is delta phi? It is a potential difference is volts. So, what is R? R is basically volt per?

Student: Ampere.

Ampere that is known as?

Student: Ohm.

Ohm right and then inverse of that usually, we call it as a.

Student: Siemens Ohm inverse.

Siemens ohm inverse, ok. Similarly, like what is the unit of kappa? This is basically volt per metre this is ampere per metre square ok. So, just note it down. So, this is basically ampere per metre square and it will be divided by volt per metre.

Student: (Refer Time: 12:08).

Right ok, that is basically electric field ok, it is volt per meter. So, the unit of kappa, what this comes? Ampere per volt metre right all right.

So, that usually now you know, what is the resistance unit is ohm right, ohm we wrote as volt per ampere right. So, you can see that volt per ampere is basically, this is ohm inverse. So, you can write is as ohm inverse metre inverse also ok. So, these are the different quantities that we usually talked about right, when we talk about electrical conductance in the sense, that electric charges (Refer Time: 12:56) what are charge carriers? Are electrons ok, you can also think in a transfer ports right.

Now, the same thing we are going to discuss for ions, what happens in solution? Ok, but just before going to that we will just discuss one very important concept, which is actually known as momentum ok. Now think about it, what we talked about conductance or just a current density, I am just start with (Refer Time: 13:35) ok.

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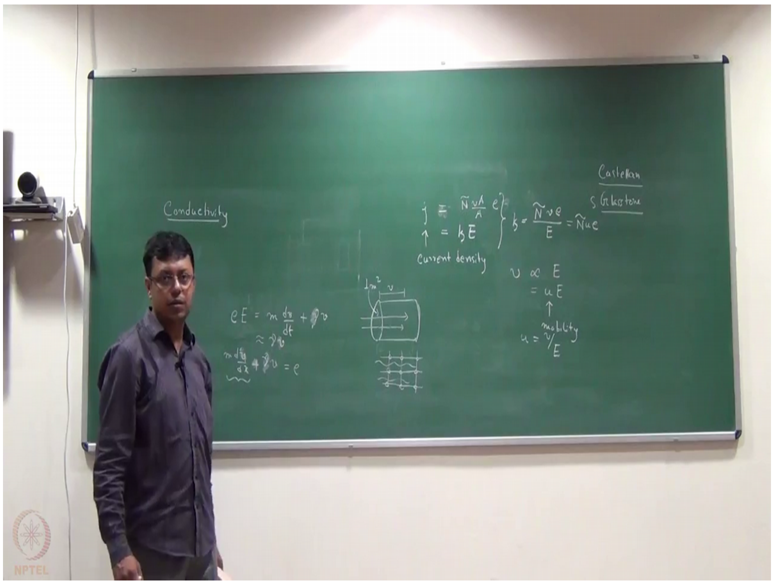

Now again, try to think about what is current density? So, suppose the electrons are flowing in this direction ok. Now current density basically tells you like how many electrons are moving per unit time per unit area right. So, it must be proportional to the density, which means like if I take say, this is suppose unit area say 1 metre square, something like that ok.

So, if it is 1 metre square and if I just take ok, let us say, per unit time it is moving say, a distance v, where actually v should be the spin of electrons ok. So, then the total volume the electrons flowing is basically, v times 1 metre square, which is basically v ok. Now that volume, how many electrons you have? If I just multiply by the density of electrons then, I will get the total number of electrons so those many electrons actually, passed through this surface each electron is carrying a charge, which is proportional to E correct.

So, then by definition my current density will be basically, the density of electrons which I am marking as N tilde times the how these come? Actually it is d times area divided by the area that is the volume right and times actually e right. So, which is nothing, but if I just write it in this way and then we also wrote that current density is nothing, but kappa into E right, we can actually equate this 2 and then we get a expression for kappa.

So, kappa is basically N v e by capital E ok. So, N is the density of the electron, v is the speed then, electric charge divided by E ok. Now think about it, what is kappa? Kappa is basically a proportionality constant right, now kappa on by itself ok, should not depend on the velocity right or basically should not depend on the electric field meaning, suppose this is the proportionality constant, if I just increase the electric field the current density is same ok.

If I have a high electric field, which is proportional to the gradient potential gradient I will have actually more flux of electron ok, but then this is the proportionality constant, this should not depend on E ok. Now see that actually, this is proportional to E 1 over E ok, but that should not happen, which means that actually within this ok, I have something which is also dependent on E ok.

Now, these electric charge this is fundamental, this density is also constant, only thing is the velocity is the proportionality meaning if I have a gradient ok, the velocity if that is also linearly proportional to electric field then, I have situation that proportionality constants have actually cancelled and then kappa is independent of the electric field clear.

So, somehow this V this should be proportional to the electric field ok. So, that fill strength and that proportionality constant we call it as mobi, we write it as mu in this case, it is mobility of electrons, but you could actually talk mobility of ions, which we are going to introduce ok. So, mobility is nothing, but the velocity by unit electric field.

You know some velocity also should change and if I just log it here, it will be nothing, but density, mobility, electric field. Now this is independent of the electric field strength, now the question is usually ok, what will be the picture of the mobility? Picture of the mobility in the sense suppose, I have electrons which is moving through like. So, emitter let us say or conductor right.

Now, usually when you write think about it, the electrons are classical then basically, there is some force acting on the electrons some charge is moving now that force think about it. Ok is basically, I can think right some electric field is there if I just multiplied by the charge and get the force right. Now that force should equate basically, the electrons motion right a electrons motion with inside a metal what could be the motion thing? Which is 1 is basically inertial force, what is meant by inertial force? Something like which is initial velocity something like Newton’s law which is basically mass times acceleration ok.

If I write it as mass times the acceleration that is basically, the inertial force the speed with which the electrons are moving and then there should be some amount, which is basically the frictional force because, if something moves in a medium ok, you always have a some frictional force ok.

Now, the frictional force is proportional to velocity, you all know right that to the motion. So, always we write that if I have a driven pendulum right. So, I have some motion of the pendulum, how we write it? So, d 2 x d t 2 or we can write it as d v d x this is basically, the inertial force ok, if there is no net force acting on the system, the particle will basically move with this right.

And then I have a frictional force or the frictional force, I can write it some constant into velocity, some people write it as with a negative sign because, actually the friction actually acts in the opposite direction, but the sign can be included inside, it does not matter ok. So that, I am just writing and that proportionality constant, some people we write it as f, some people write it as the standard notation is gamma and those force is basically, equivalent to the external force, if there is an external force. In this case, the external force is created by the electric field, I applied the potential difference ok. A negative gradient of the potential is equivalent to the electric field and then if I multiply with the charge, I will get basically the net force ok.

Now this is basically the equation ok, equation of motion, but now think, about it if the velocity has to be proportional to E right. This term will be very small ok, it is mostly dominated by this gamma into v ok, this is basically the frictional force and then actually, we can make an analogy ok.

Now, what is the origin? Basically of this velocity being proportional to the electric field, because, if you apply more and more field, if you think about it, ok. There is a inertial force, that is not changing ok, but then the electron is experiencing more and more friction as it is as it is moving more it is basically, colliding with the ions in the crystal that is ok, you can think that electron there is basically, some valence electron which are in the conduction band right.

And then if I have electrons in the conduction band, left things are basically ions. So, I have in the crystal like this I basically, have ions left which are atoms minus electrons right and now this electrons are moving basically and then they scatter with this ions and that scattering basically gives rise to friction and on based on this model there is a whole thing of electrical conductivity we will start discussing about first a classical model which is known as a Lorentz Drude Oscillator model ok, I am not going into the details ok.

And then talks about the limitation of the model why the classical model is wrong? then you can think about the particle in a box model and then you can actually modify all these models ok, those actually explain electrical conductivity ok, we will not going to the details, but we will have to be introduce the similar concept for ions, where I will also say the ions velocity will be actually can be replaced by something known as the mobility ok, which is basically when the ions are moving per unit field gradient or sorry, potential gradient or basically per unit field all right.

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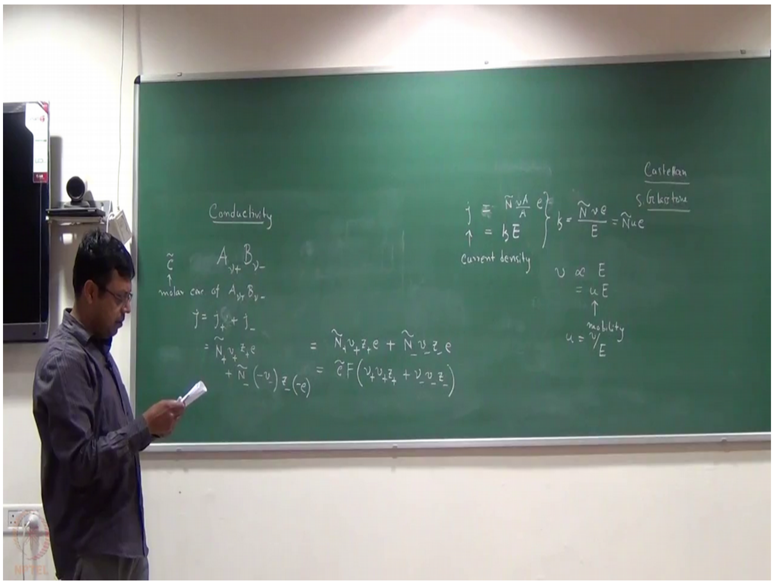

So, now let us talk about ions now again just think about, let us say electrolyte I am writing it as the electrolyte as A nu plus B nu minus ok. So, the charge on A, I am assuming that it is Z plus and charge on B is basically, Z minus ok. For example, let us say anything I just take an example arbitrarily say Fe Cl 3 ok. So, nu plus here is 1 A is iron and B is chlorine right.

So, nu plus is 1 nu minus is 3 ok. So, z plus is basically plus 3 z minus is minus 1. So, (Refer Time: 23:40) of course, for electrical molarity, I should have nu plus Z plus must be equal to (Refer Time: 23:46) is a subscript. So, nu plus Z plus must be equal to nu minus E minus ok, that is the condition for electrical conductivity clear all right.

Now, the question is what is the current density for this species? Ok, in the simi[lar]- in the very similar ok. Now think about it, in this case ok. So, the cations are moving, suppose in this direction ok. So, the anions must be moving the other direction right. Now the cations, which are the cations is basically A Z plus right and the anions are basically B Z minus ok. Now think about it, when the cations are moving those are carrying positive charge towards it ok.

Now, if I add the current density only for the cations, I have to write only cations are there the number density of the cations in the same like N times the velocity times electric field something same ok, but in this case actually, I was carrying charge E right and in this case, it will be Z plus nu ok. Now that charge is being carried for the anion now it is very interesting. So, let me we just write it first ok. So, basically it will be carried by cations plus, it will be carried by the anions right.

So for cations, I am just write, the same way I just write it as N plus. So, I am just writing the current density, I write it as N in the plus and A and A will cancel then v plus and then I have basically z plus into e well. So, that is moving in this direction for anions actually, these are moving in the other direction ok, but let me just write it in this way anions say N minus of course, N plus and N minus will be different because, it will depend on a (Refer Time: 26:05) if nu plus and nu minus are same then actually they are same otherwise they are different.

So, for anions I have N minus now if I take v plus as the positive direction I have to take the v minus as minus v minus because, it is moving in the other direction and then Z minus by the charge, this is also not e it is minus e because, it is anion ok. So, together as see that these 2 negative things cancel ok. So, it is as if cation plus anion together why it is happening? It is very simple to understand physically like, I have positive thing moving it is equivalent to negative thing moving in the other direction ok.

So, overall there is a positive thing moving in this direction, which is contributed by both positive ions as well as negative ions moving in the other direction clear just like, in conductors you always say that electron is moving, but you could have thought the same thing as holes are moving in the opposite direction. Here actually, both things are moving cations, anion both because, both are mobile.

So, we can actually write it as basically N hat N tilde plus v plus Z plus e plus v minus Z minus e clear all right. Now, think about it like suppose I took the initial concentration of this compound as say something, let us say C tilde ok, now what will be the N plus? N plus will be nothing, but it is basically is a molar concentration let me just write it, this is a molar concentration of this compound, which is A nu plus B nu ok. So, what is my n plus? N plus is basically total density, it is not a molar density because, we know that was basically volume times the number density ok.

So, if I have this many moles if this is the stoichiometry, each mole will give me nu plus cation right. So, the number of moles of cation will be nu plus times C those many moles, if I multiply by Avogadro number then I will get the number ok. So, I can just write it, we can take something common in both cases as you can see C will be common because, actually I am going to replace this n plus as C times Avogadro number times my nu plus ok.

Now, I will be left with this Avogadro number times e that is also common that is nothing, but F ok. So, what I am I am going to do? Is basically, I have C and F those will common clear and then inside, I will have N plus I replaced by C times Avogadro number ok, times nu plus. So, in inside bracket I have nu plus v plus Z plus e already I have taken inside F plus, I have nu minus v minus Z minus clear all right.

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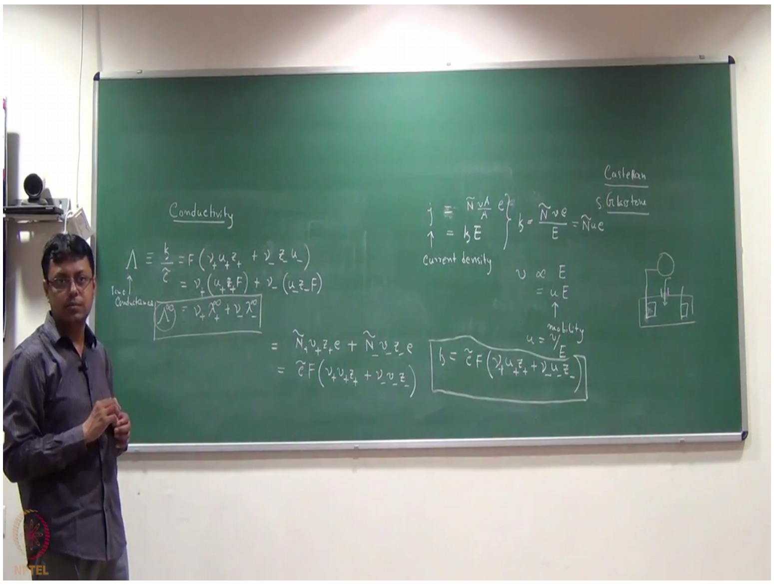

So, again instead of like, so, basically this is the formula for current density ok. So, what is the formula for kappa? Kappa is nothing, but j divided by E right, if I had divided by E ok. So, v plus by E I can write it as u plus and v minus by E I can write it as u minus. So, the corresponding formula for the kappa will be is C tilde F nu plus u plus Z plus nu minus u minus Z minus clear all right.

Now think about it, what term usually I wrote the conductance there as L right. Now that is usually, preserved for electrical conductance for electrolyte conductance we usually use the notation as lambda the Latin equivalent of L capital lambda, there actually we are writing capital L. So, this is the same thing, how this is the conductance? That in this case this is actually the ionic conductance ok.

Now, what is ionic conductance? Ionic conductance just in the same way right, we had basically, you could remember I had kappa and I am saying per unit concentration, what is basically the conductivity ok. So, that is defined as kappa divided by per unit basically molar concentration ok.

Now, if I define I have defined this thing ok. So, in terms of my equation, what it will be? It is a straight forward. So, which is divided by C tilde ok. So, just have F times nu plus u plus Z plus times nu minus Z minus u minus. Now sometimes, it is also written as now as you can see here, what I have here? I have lambda which is kappa divided by C tilde which is basically F nu plus u plus Z plus whatever now think about it, if I just take if I just write it in this way u plus Z plus F.

So this again, we will have dimension of something like lambda because, this is just a number ok. So, then this quantity we call it as basically, the contribution of lambda, which is ionic conductance, which is given that cation ok. So, we write it as something like nu plus lambda plus and nu minus lambda minus clear.

So basically, I have conductance ok. So, this is the overall conductance, this is again the overall concentration this is the overall kappa of the solution, which is contributed by both the cations and as well as the anions and I am basically dividing it into 2 parts this is just a notation ok.

Now, the this treatment was done by Kohler's and he basically, said that whenever you talk about electrolytic solution you have to talk about both cations and anions, this is basically following the Arrhenius, this theory of electrolyte dissociation ok. Now so far, the way we have drawn it we have not talked about, what is the like degree of dissociation, whether this is like for sodium chloride or FeCl 3 or some something like acetic acid because, acetic acid will not dissociate completely ok.

So, you can make a connection we will come to that ok. So, how many cations are there? How many anions are there? That we can make a connection and then actually, we can measure the conductivity ok, now the problem is that this formula ok. So, when little like write it the total conductance, I can write it as conductance of cations and conductance of anions because, these are 2 parts right now it is kind of inseparable in the sense, that what you will measure? You will measure the conductance right.

The conductance is a physical quantity that we have already discussed right that, I can always mention right how I measuring. So, like say ionic conductance I can have basically 2 electrodes ok, which is deeply solution and then I can make a (Refer Time: 35:10) actually I can filling the solution and then what I will have? I will basically measure the resistance not people usually do not measure, the conductance ok. So, it will be adding add as to some like resistance conductivity, how you measure like Wheatstone bridge ok. So, if I just attach an Wheatstone bridge here, I can actually measure the resistance and from the resistance, this is basically the reciprocal of it is the conductance that is how I can measure it ok.

Now, the thing is that measurement in the governs give me this thing and then I have no clue, what is lambda plus and lambda minus? Clear. So, that will be a difficult thing to do if I can actually solve it for individual lambda plus and lambda minus ok. Now the second thing here, is that think about this conductance now I told that la[mbda]- as of now here ok. So, this is independent of actually concentration because, this is by definition per unit concentration how many? Ok, what is basically the conductivity? Ok.

But suppose I am bring the conductivity measurement and then what I did? Is basically, I suppose use concentration of different like say for example, (Refer Time: 36:36) and I am taking different concentration ok. Now this equation is telling me actually, the conductance should be same that in practical in practical it does not why? Because as I am actually concentrating the sample ok. The movement of the cation actually is influenced by the movement of the anions right because, these all these derivation whichever I did the cation, anions speed are not influenced by each other clear, but at a very high concentrated solution ok.

If I have too many cations basically, what will happen? They will basically surround the anions and anions are also surrounded by the cations ok. All these things will happen and then that will definitely affect the velocity ok. So then since, everything is depend on the velocity, when conductance should change. So, in principle these 3 should hold, when the cations and anions are independent velocities and that will happen if the solution is kind of infinitely diluted ok. So in other words, we usually write instead of writing it in this form, we always write a notation, which is like this lambda infinity which is basically lambda plus infinity and lambda minus infinity ok.

So, these are basically the infinite dilution only that since, we can actually write that cations and anions are independently contributing, I can actually add them otherwise I cannot add ok. I will show you the experimental curves ok, but before that let me tell you one more thing, I have written actually. So, we wrote it as (Refer Time: 38:56).

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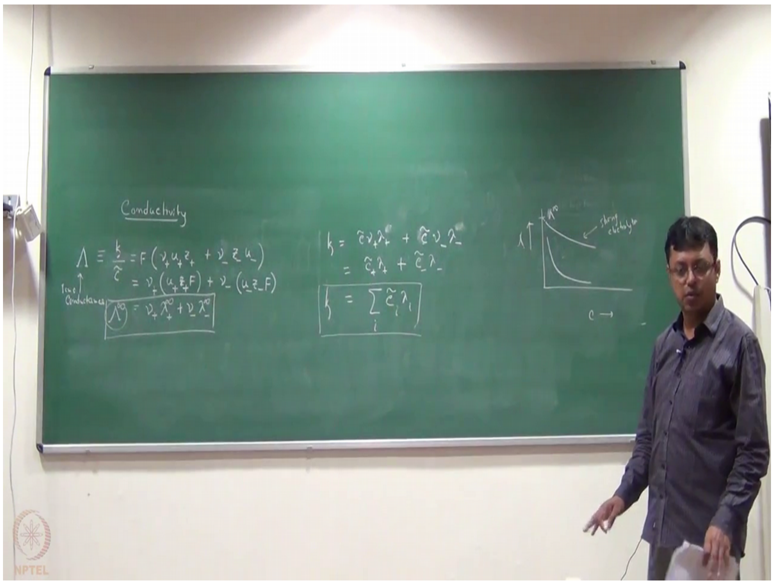

So we can actually write it like this, this kappa is nothing, but I wrote it as C tilde plus this one. It is basically C tilde nu plus lambda plus infinity, what is C tilde? C tilde is basically the molar concentration of the substance right, now which means actually C tilde plus into multiplied by nu plus is nothing, but molar concentration of the cations ok.

So, which I can, I could have written it as C tilde plus lambda plus, let me just not write the infinite thing that is basically for like, ideal condition; so that means, I can just drop it the infinite ok, but of course, this thing only hold for infinite thing and then I can write it as C minus lambda minus in general like, I could have written as kappa is nothing, but all the Cs and their conductance the summation ok. So, this is basically a compact notation for what is known as Kohlrausch's law ok.

Now, the interesting thing here as you can see there are 2 things, one is basically I can only basically multiplied this nu plus with C to get a C plus now there is basically C, I now suppose I have something as now suppose I have say acetic acid or say some acid base in water now what will happen here? All of you know that if I add kcl to water ok. So, what are the species? So, far we are considering like cation and anion, which is 1 is to 1. So, I have K plus I have Cl minus, but what also does after dissociation right. So, I always have OH plus and OH minus actually the species is H 2 o plus, but I have write is as H plus ok.

But then my KVR is actually 4 not just 2 ok. So, even if I am actually adding 1 is to 1 electrolyte ok. I should use the generalized equation in the sense like, what I am trying to see here is that if I have say let us say anything like, KCL or NACL I have to actually write it as something like this lambda H plus and then I have OH minus lambda OH minus then I will have the cation and anions ok, but these part actually, I cannot ignore then usually some people will actually write it as basically, the conductivity of the water ok.

Now, that is why one need to measure the conductivity of water ok. The water has to be ultra pure you always use basically de-ionized water because, if it is a ionized ions are present that will itself show conductivity ok. Secondly, to get that actual values you have to anyway that use the dilute solution because, this is this equation holds only for the infinite dilution or in a very dilute (Refer Time: 42:32) ok. So, then if you actually try to full fill those condition your water has to be very ultra pure ok. Now what usually people do is that you take the conductivity and you measure the waters conductivity separately, you take the subtraction K minus K w and that will be basically equivalent to the conductivity of contributed panel, I am shown ok.

But again, this is not very correct because, the presence of the ion can also increase or suppress the dissociation of water ok. I am assuming that, the water dissociation is independent of the presence of the ion ok. So, without the ions whatever I am measuring have the contribution of water is the same in presence of the ion, but that is not a correct thing, but people usually do it ok.

And then the other thing is that, we can always do basically, the measurement of the conductance versus say concentration. Now for strong electrolytes something like say, potassium chloride or something like this we get a more or less linear curve ok. Now, we can see that this actually, decreases with concentration because as I am increasing ok. So, what is happening is that there are more number of conductance which is slowing down the mobility ok.

So, of course, you cannot actually get an infinite dilution, you always try to fit with a non-linear equation and try to extrapolate it to get the lambda infinity. Now this is the typical thing for strong electrolyte ok, for weak electrolytes actually we have a very different curve for electrolyte, this will be very sharp dependence why? Because you know why, if I actually increase the concentration the degree of dissociation will be now, less ok. So, I will have a very sharp fall something like this and which one you cannot extrapolate it now that is the problem ok.

Now how do you tackle this problem? That is the question ok. So, what all right now what we discussed is that for weak electrolyte how do I measure lambda infinity or basically, the infinite dilution limit conductivity? Ok, where I can actually get this identity thing cations plus anions ok.

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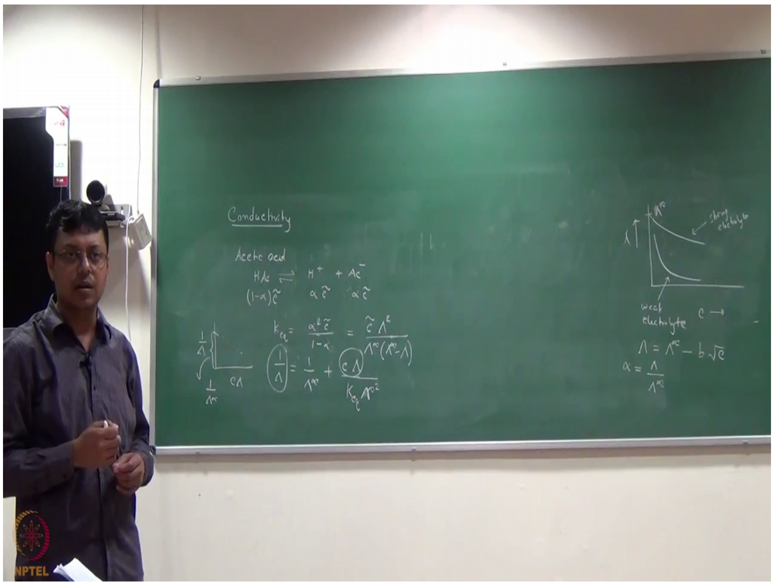

Now we can actually, consider some let us say acetic acid ok. Acetic acid usually like I am just writing it as H acetate. So, this is the acetate and this is the proton and which of course, can dissociated with H plus and AC minus right and suppose the degree of dissociation is alpha ok. So, if I have 1 mole here when it is dissociated, I will basically left with 1 minus alpha and 1 alpha here and 1 alpha here right ok.

Because, the alpha if the alpha mole gets dissociated, I will have alpha there right and if I had basically, C tilde concentration and basically alpha C tilde alpha C tilde clear I will show you for any that fixed temperature of course, there will be there will be an equilibrium know and the equilibrium constant, we can write it as the degree of dissociation and then you can easily see, it is basically alpha square C square right divided by 1 minus alpha into C 1 C will get cancelled ok. So, I will basically get alpha square C divided by 1 minus alpha ok.

Now, there is an empirical relation, empirical relation in the sense like this curve as you can see here you can actually fit as I said that you can actually fit it with some standard, non-linear equation and you can think that this thing, which is basically for weak electrolytes can we approximate it as lambda? Is something like the infinite value thing and then it basically decays as a function of square root of C, which I am actually use a proportionality constant, but this is actually one type of form, which actually acetic acid shows maybe a formic acid or some other acid, may show a completely different non-linear form again, this is the. So, it is called empirical field ok.

Now, one can also like kind of say ok. So, this degree of dissociation is actually equivalent to something like, lambda divided by lambda infinity. Now this was basically suggested by (Refer Time: 48:00) ok, where he said you can think of it like if the degree of dissociation is 1 then my lambda is equal to lambda infinity, which make sense. Now when the degree of dissociation will be 1 when actually I have infinite dilution so that 1, if you think then actually in that limit actually it holds only for the not only weak electrolyte, but in a very dilute condition because of course, I more than this is a non-linear function, but still I am actually trying to make it kind of linear ok.

If I use that here then, what I will get is semi equilibrium constant, but I will basically, write this instead of alpha, I will just write lambda by capital lambda I lambda I infinity ok. So, it will be basically lambda square by lambda infinity something like that, it will be 1 minus lambda by lambda infinity ok.

Then I am just basically dividing both side numerator and denominator by lambda infinity square ok, if you do that. So, what I will be having? I will have the C tilde ok, then I have lambda square, I have lambda infinity square at the denominator right, here it is basically lambda square by lambda infinity square here, I will have 1 minus lambda divided by lambda infinity, which I can write it as lambda infinity minus lambda divided by lambda.

So that thing we will yet not written. So, I will have this, it is just after the electron clear all right. Now the interesting thing here, actually the question is how will you get a extrapolated curve? That was the initial problem right for an weak electrolytes. Now I can actually solve it, how we can like instead of plotting the lambda versus C I could have actually rewrite this equation as this.

So, this is just a another way of writing this equation ok, we can easily figure this out, this is basically, I am just took the 1 by lambda if I plot 1 by lambda versus this thing then I see that there is the straight line ok. I could have actually plotted that and from that actually the if I measure the slope and the intercept ok, I can easily get the equilibrium constant and from the equilibrium constant, I know the degree of dissociation that way, I can show actually I can calculate equilibrium constant and the 1 by lambda is basically, the intercept 1 by lambda infinity ok.

So I can actually plot different one this I could have instead of plotting lambda versus C, I could have plotted these 2 constants and then actually, I have a negative slope and then the intercept we are defining basically, the one over lambda infinity that is one of the way, one can do and this is something you already know something like say for example, second order rings ok, you always plot 1 over A versus 1 over A 0 ok. Similar concept actually instead of plotting it non-linear function, I can always get a linearized function and then to a linear fitting ok.

But then I am not plotting the same quantities, this is not concentration versus time it is a reciprocal of concentration versus time that way, you can do it or the non-linear functions something like that ok. So, that you convert it to a linear curve similar thing, you can also do here alternatively, I will show you that we can also could have actually use the Kohlrausch’s is a very interesting ok.

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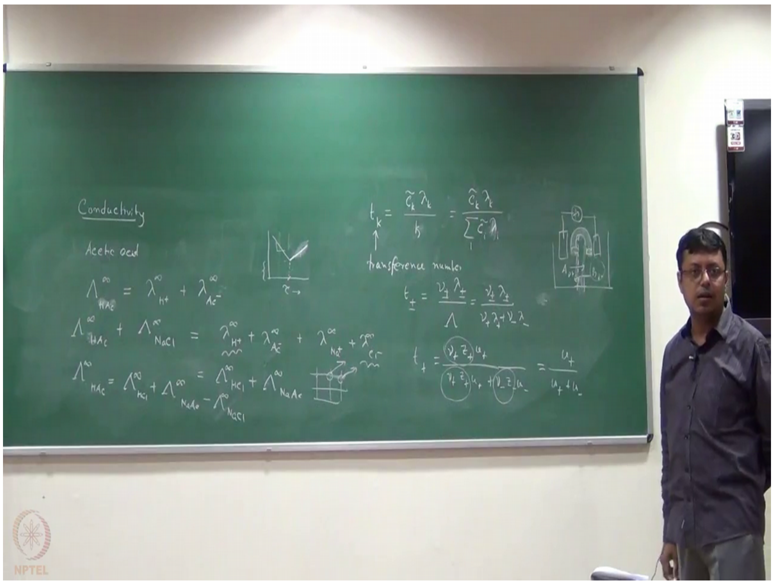

Now, what we have? Is something like say for acetic acid, which is ACH ok. Now I know that is contributed by what that is contributed by cations and anions right. Now I wrote remember it is basically, nu plus into lambda plus the nu plus and nu minus always 1 here because, it is just 1 is to 1 electrolyte ok. So, I have basically, lambda plus ok, but plus is basically nothing, but H plus here right and I will have lambda minus which is nothing, but AC minus and these are all I am talking about say in the infinite dimension ok.

Now, there is a interesting thing that suppose, I have acetic acid and plus say something else, let us say NaCl ok. So how here how you can write it? So, lambda acetic acid I was writing it as instead of ACH, you can write it as HAC on the infinite dimension ok. So, I can write it as lambda H plus and for NaCl ok. Suppose, I use basically acetic acid along with NaCl ok both are sufficiently dilute so that, I can write it as if it is infinite here ok. Now there is a trick, trick is that I want the acetic acid thing ok, lambda NaCl, I can know I know, how? Because it is a strong electrolyte, the curve not so non-linear. So, I can actually extrapolate and get that part ok.

Now, I know in that infinite theory ok, definitely it is contributed by the cations and anions ok. So, acetic acid is contributed by H plus AC minus, this is contributed by NA plus and this thing Cl minus. Now what I am doing? I am now doing a very interesting thing. Look at it this thing, if I add this is nothing, but basically conductance of HCl that is a strong electrolyte and these 2, if I add that is sodium acetate that is also strong electrolyte ok. So, this is nothing, but lambda infinite HCl plus lambda infinity of NaAC ok.

Now see, this is strong electrolyte, this is strong electrolyte, this is also strong electrolyte. So, I can actually go back and measure the weak electrolyte without measuring it clear ok. Because, everything is strong. So, nothing I will have basically the lambda infinity of acetic acid is nothing, but I could have taken HCl measure the infinite dilute concentration, I could have taken the acetic acid measure the infinite dilute concentration and I am just subtract from these values ok, this is the infinite dilution conductance of NaCl ok.

But again, this is true for only 1 is to 1 thing. Of course, if it is complicated like we should have actually written nu plus nu minus ok, but then you have complication because otherwise, the stochiometry should match ok, but this is one of the very interesting way ok, I do not need to actually measure the weak electrolyte, I will just measure 3 strong electrolytes, which I can easily extrapolate ok and from that extrapolation I will get all these values and those values combinations will give this thing ok and this holds because, that Kohlrausch's law was additive in the infinite dilution, not in the general thing ok and since this was additive, I can always spread things ok and put it together ok and separate it clear.

Now, we just discuss the last thing, which is known as transport number or transference number. So, basically, the transport number, if conductivity of order is mean or sometimes, this is mostly known as the transference number. This is defined as the concentration, suppose is K of a particular species and divided by this is called kappa and kappa already you know that it is nothing, but C i.

So, this is basically known as transport number ok. Now transport number of the Kth element ok, suppose I have sodium chloride, potassium chloride and only water ok. So, then I have many species here ok. So, transport number of a basically a particular ion is defined as (Refer Time: 58:20) what is this C plus? C into lambda ok, sorry this should be lambda.

Now, what is this C into lambda? C into lambda is nothing, but some measurement of conductance already, we have discussed right. Now, these basically tells me what is the total -[trans] portation and this is basically conductance contributed by the particular ion.

So, transport number gives you a kind of fraction or the contribution of a particular ion towards the total conductance clear ok.

Now, it depends on many factors as I said like in the like say sodium chloride ok. Now you cannot just say like, which one is contributing more, it depends on many things, not only just concentration because, concentration same here it is same. So, 1 is to 1 electrolyte I have same number of sodium ions and same number of chloride ions ok, but what makes the difference? Is basically the mobility, which is velocity per unit potential gradient or unit field, right.

So, ultimately actually, everything is limited by the how fast or how slow the cations or anions are moving? If it is a fast moving thing then actually, it will carry the charge more, clear ok. So, that is basically known as the transport number, which is basically the in perhaps only electrolytes, ok. So, then the fraction of the charge ok, carried by a particular species is known as transport number all right.

Because I know that C times lambda is nothing, but some kind of conductance ok. Now, I can actually write an equation for transport number only for 1 is to 1 the electrolyte ok. 1 because, let us say suppose, I have a cation transport number ok. Now cation, how will you write t plus? So, t plus will be nothing, but. So, this is what? It is basically, conductance ratios right.

So, what will be t plus, anybody? This is only nothing but say, nu plus lambda plus divided by a total conductance, ok. Similarly if I write t minus, it is just minus here ok. As you can see that t plus and t minus will be equal to 1 ok of course, it make sense because it is a fraction out concentration ok.

But of course, t plus and t minus in this case actually right to 1 is to 1 electrode ok, electrolyte. Now we could actually, modify this equation little bit, in the sense that, I could actually write it ok. Lambda plus and lambda minus, I could have written as these things ok. Already we will rewrite, all these equations right, you have to specify Z plus into nu minus nu plus right.

So, if I just write it, what I will have? It will be basically, nu plus Z plus nu plus and in the denominator, I will have nu plus Z plus ok u plus and nu minus Z minus u minus right. So, now, you see what I have? Let us say just write it for cation. Say, t plus equal to nu plus Z plus u plus divided by nu plus Z plus u plus and plus mu minus Z minus u minus. Now what is nu plus z plus? nu plus is the stoichiometry, Z plus is the charge. For electrical neutrality, these and this should be equal right. So, these 3 things are basically important ok. So, the transport number is nothing but, the ratio of the mobility to the cation mobility ok. If we had taken the minus, it will be basically u minus divided by u plus and u minus ok.

So, transport number is directly connected to the mobility. So, that is what I was telling like, fraction of the charge, which is carried by the cation and anion is not dependent on the numbers, it is ultimately connected to the how they are fast? Ok of course, it depends on the number like say Fe Cl 3 ok, if even if the chlorines are slow ok.

Suppose, I do not know actually whether iron is slow and chlorine is slow, most likely the 3 Fe 3 plus are slower ok, but suppose if Fe 3 Cl minus are slower ok, they can still overcome because, I have actually 3 ok. So, this will of the I mean this will hold in a different case basically, when I am I have everything controlled by only mobility clear ok on the speed of the anions ok.

And there is a very small discussion on conductivity titration, which everybody knows like if I actually do an acid base titration based on conductance ok. So, what will happen? Like if I just suppose, I am doing a titration ok. So, suppose initially in the solution I have something let us say, I have base ok. So, the carrier is basically OH minus right and as I am neutralizing ok.

What is happening? Basically the conductance should drop, usually for strong electrolyte, we said that it is kind of linear. It would not be exactly so much linear and then it will drop and then, if you add excess right then the acid will basically, become the conductor ok and then of course, the slopes are kindly different because, the contribution by the anions are different from the cations, because OH minus and H plus mobilities are different ok.

And this is basically if I do a titration ok. This will, basically equivalence point at the equivalence point actually, I have non 0 conductance why? Because, neutral water also conducts, ok. So, there will be some residual conductance always and that will always do ok all right this conductometric titration.

So, there are some discussion on conductometric titration here also and but just as it is summary why this part is very important? Is the where the mobility of the ions are so important again, this is a very like simplified model of ionic conductance ok. It just takes into account that the velocities are independent again ok, which should be true at the infinite calculation limit and the second thing is that always written like that in many technological applications.

For example, let us say a lithium ion battery ok, the major charge right now is basically, when you do this charging discharging cycle ok what happens? Is that you have basically, this is solvested battery right and you have some layers and between the layers, I actually have the lithium ions. So, I actually pull out the lithium ions and then, I move it back ok. When I am doing it. So, lithium ions are basically, interconnected inside the layers right. Now there are 2 things, one is basically the mobility of the lithium ion ok, how fast and how slow? Basically doing this charge and discharge ok.

But every battery has a lifetime, the reason is when you are actually putting back the lithium ions right, all the ions actually do not go back and perfectly sit ok because, when you move out something like suppose, I have a crystal I have a some lines form and now suppose, we are actually removing the ions out and when I am bringing them back they may not fit into the same side ok.

There may be some defective way of arrangement ok and it will increase with the number of cycles and that is one of the challenges ok, you connect a lithium ion battery technology like, how will you track the ions, when you are doing actually the discharging cycle ok, when the ions are basically coming back and fitting and then basically, this structure gets disturbed the interconnection is not doing very perfectly ok.

So, the mobility of the ions are very important in that sense. Secondly, which I did not discuss, due to this difference like suppose I have like a condenser think about it ok. So, 1 electrolyte is here. I have a electrode, I have another electrode here and if I connect it ok of course, I have see anything, because I have to move the ions also right and to move the ions, what I do? Is that I will actually connect it as a as something known as salt bridge right and interestingly, what a salt bridge does suppose if I do not have a salt bridge and what I am doing? Is that I suppose I have a some kind of arrangement across, which the ions can transferred ok.

Now what will happen? Suppose the cations, which we wrote as A nu plus minus and suppose the anion nu minus they are moving, but they have different velocities. Suppose I have my nu plus and nu minus are same like, same number of cations and anions are present ok, but since the mobilities are different ok as the current is passing maybe suppose the cations move faster ok.

So, what will happen? Actually I will not, I will not have actually electrical neutrality in the solution, I will develop a potential across this weight, this is known as liquid junction potential right. So, this is basically an acid, this is a liquid junction and I am developing a potential in the solution ok and if I keep on doing extracting the electron, I will come I have actually more cations here, more anions here or less anions here ok.

Then this, extra cations will actually stop, the new cations coming in ok. So, what is happening? Ok anyway. So, then that will basically, reduce the flow clear ok. So, in order to actually make this thing continuously happen, I have to actually remove the thing ok. I will remove basically the potential electrons and that is why, what we will do here? Is that use a basically known as a something known as a salt bridge ok.

Now, what is slat bridge, does? Salt bridge actually provide extra ions right, which are actually same for cations and anions, which basically have similar mobility so then, actually your original cation is not reaching there, it is basically original cation is reaching up to the salt bridge and from the salt bridge some ions are going ok. So, that it always maintains this electrical neutrality.

So, salt bridge basically removes the liquid junction potential, all right there is a some discussion in electronics book also and based on that you can also develop something known as concentration cells ok, where actually, you could have actually started with the different concentrations ok and then, you can actually get some electricity out of those cells. So, we did not discussed those things ok.