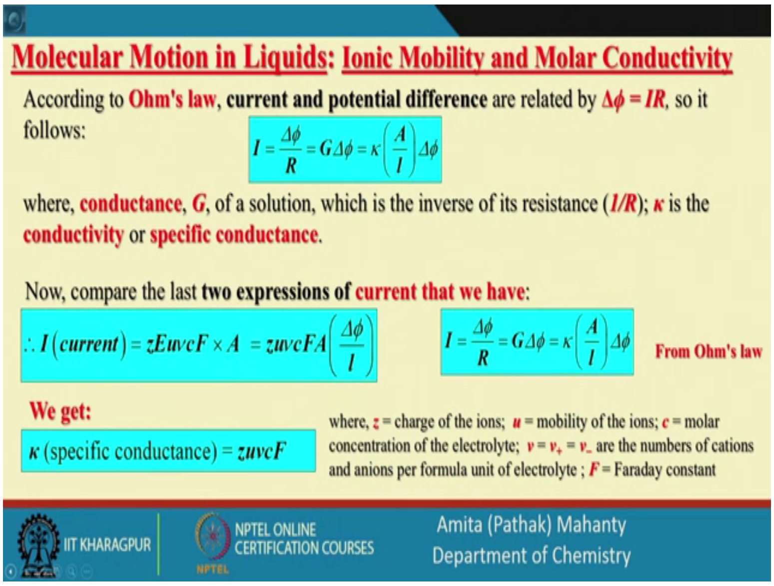
Molecules in Motion
Prof. Amita Pathak Mahanty
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 23
Molecular Motion in Liquids (Contd.)

Ok Welcome to another lecture on the Molecules in Motion.

(Refer Slide Time: 00:21)



In the last class what we were talking about is the ionic mobility and the molar conductivity. In that we had derived expression for current as the ions were moving across electric field. What we had talked about in the last class, that whatever we derived, we will see whetherthe Ohms law, which is supposed to bevalid in this very dilute solutions of the electrolyte and whether the Kohlrauschs law of independent migration of ions are valid.

So, starting from the two expressions we last talked about was the two expressions of a current. So, starting beginning from there let us see if we talk about whether it is Ohms law is valid or whether the Kohlrauschs law is valid from the expression we are going to validate that.

So, according to Ohms law what we have? If you have a current and a potential difference current I the potential different phi and delta phi, then the potential difference we say the voltage is equal to I R. So, the current is equal to v by R. So, if v by R here I am expressing the v as the potential difference across the two electrodes that is delta phi by R.

We had derived this in the last class that it is equal to G into phi delta phi, where G was the conductance, which is inverse of 1 by R. So, from the expression of the conductivity or specific conductance, which was; otherwise known as kappa, this expression of kappa if you can look into then we can say that kappa into l by A into delta phi.

So, current which we have derived as v by R from the expressions of Ohms law if we go into terms of whatever we have derived in terms of the conductance that is it is going to be the specific conductance or conductivity into l by A into delta phi this comes from the expression of G G is 1 by R.

So, and kappa is 1 by R is G and from there we put the expression of kappa. kappa is equal to a kappa into l by A into delta phi gives you the I. So, A is the cross section area of the electrode and l is the length between the two electrodes.

So, if we see this expression and another expression of the current which we had derived in the last class, what was the current expression which we had? This was the current into the total area, this was the current a flux of charges into the total area was giving you the current.

And here we had replaced the E the electric field in terms of the delta phi by l. So, this E is if we replace this E the electric field by delta phi by l then the expression becomes something like this.

Where you can see what is the z. Z is the charge of the ions, u is the mobility of the ions and c is the molar concentration of the electrolyte which we have used. And mu here we have taken in the last expressions we have simplified and taken only nu.

Where we have taken that nu plus and nu minus is equivalent to nu because we are taking a electrolyte we did not differentiate between the separate ions. But we have to understand that we whenever we are doing the contribution we have to take the contribution of the plus and the minus ions individually.

So, what we have here a nu is the number of ions or cations or anions per formula unit of the electrolyte. So, if this expression you have for current this is the area which we are looking into of interest. The area of and the window we are talking about.

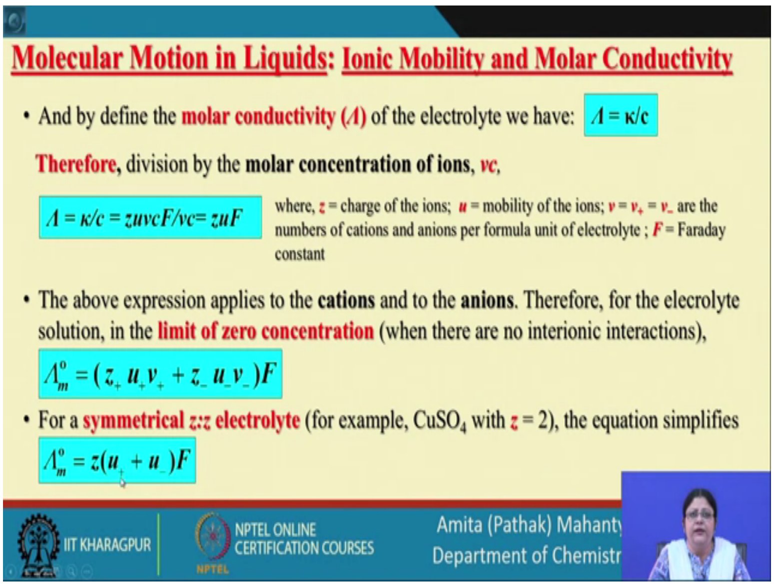
So, if this is the current which we are looking flowing through the system and we have not I have another expression of current from the Ohms law. I we can equate the 2 I's from the 2 expressions what do we get? You see this phi and this phi is going to be phi by can be taken to be common. Then what you have, you have the A common.

So, if you separate out this part and you separate out this part then what you have is remaining is the z u v into c F. That if I compare that with this expression then that should be equal to this conductivity or specific conductance.

So, specific conductance kappa or in conductivity kappa is equal to the z u nu into c into F. F is what is the faraday constant and c is the molar concentration nu is the number of cations or anions respectively for a per unit of the electrolyte. And z is the charge u is the mobility of the ions.

So, what we have related we have related the specific conductivity or specific conductance kappa with the expression which can be of interest this is the mobility. So, this is the expression which is connecting the specific conductivity and the mobility of a particular electrolyte.

(Refer Slide Time: 06:22)



Now, the molar conductivity gamma, lambda, capital lambda of a electrolyte is nothing, but kappa by c. And if I looked into the expression of the kappa, this is the kappa I have by c.

What is the c here the number of ions molar concentration of the ions if nu is the number of cations or anions per unit electrolyte. Then the number of ions the concentration of ions should be that many number into the molar concentration, which is existing for the electrolyte because the electrolyte is going to give rise to the same number of cation and anion in a system, when we are concentrating on a single electrolyte system in the consideration. So, lambda the molar conductivity or molar conductance is nothing, but kappa by c and here what will be the c here? At c will be the concentration of the molar concentration of the ions. Molar concentration of the ions need to be taken into the number of ions which is going to be per formula unit of the cation or anion which is going to be generated.

So, if you divide the expression which we have for the kappa divided by the nu c the molar concentration of ions ok. Molar concentration of ions will be nothing, but the nu into concentration. That concentration of the electrolyte is c the molar concentration and this is the number of formula units of the cation and anion which is going to be generated.

And that should be the total concentration of the ions in the system. So, if I divide by the total concentration of the ions, then what I have is the molar concentration; molar conductivity and that is simplifies to z u F.

So, we have a expression where previously I was equating it with the specific conductance now I am equating it with the molar conductance. So, molar conductance expression comes to be lambda equal to z u F.

So, u is the mobility of the ions, now I can take that to be contribution of the plus ion as well as the negative ion. Here we are equating plus ion to be equal to the negative ions and that I have represented by u ok.

Now, the above expression which you have the above expression applies to the cations and to the anions. Therefore, the electrolyte solution in the limit of concentration zero, means in very very dilute solution where there is no ionic interactions inter playing in the solution. Then what we can have then? We can have the molar conductivity or molar conductance at infinite dilution equal to from this expression.

I have the contribution of the plus ion into the mobility of the plus ion into the number of plus ions generated per unit formula, plus the negative ions. The conductivity of the negative ions and the number of formula unit of the negative ions generated into F.

So, what we have come down to? We have come down to the expression of molar conductivity we started from the Ohms law expression. And equated that how the Ohms law if we equate the current from the Ohms law and what we have derived from the expression.

So, far for the current those two current expressions were equated. And then we got a expression for specific conductance from there we found out that expression for molar conductance.

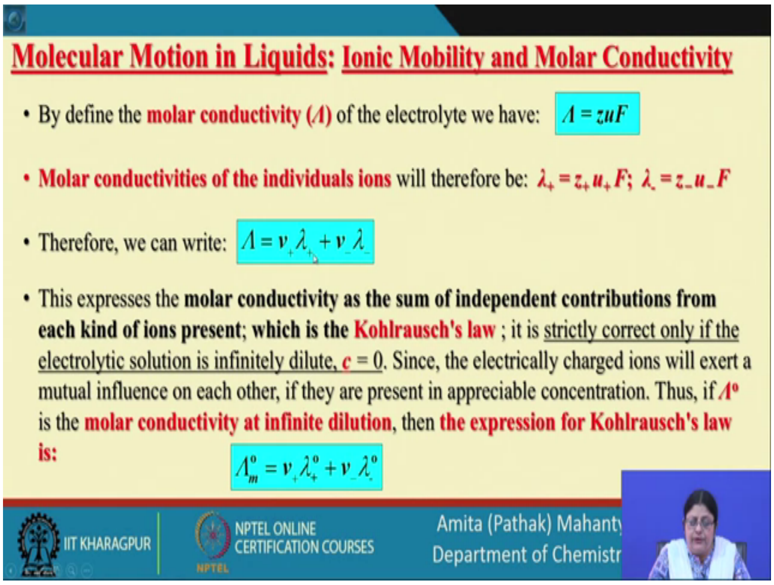
Now, from this molar conductance when I have writing it like this, when I say that the ions are the solution is very very dilute in the limits of zero concentration. When there is no ionic interactions playing, then I can take the contribution of the plus ions and the minus ions in the electrolyte system.

And hence can rewrite the expression of the specific the molar conductance as the lambda at infinite dilution equal to sum of the two cations and anions in terms of the charge as well as the number units they are generated into the mobility of each of the ions. This is something which is similar or familiar with that of the Kohlrauschs law of independent migration of ions ok.

Now, if this expression can be further simplified if we say if you have a symmetric z z electrolyte 1 1 electrolyte like k c l. And if we are talking about 2 2 electrolyte it can be copper sulphate. The equations simplifies because the z equal to will be equal in both the cases for cation and anion.

So, z can be taken out and then you have u plus the u minus. So, for a symmetric electrolyte this is a generalized expression which can this generalize expression can be rewritten in this form ok, this is a special case which we are looking into.

(Refer Slide Time: 12:05)



Now, by the definition of molar conductivity what you have lambda equal to z u F ok. When we have not separating out them into the cation and anion, but molar conductivity of the ions, individual ions if you want to take then we take it for the positive ion.

And each of the ions will be represented by the z plus and u plus for the positive ions and the lambda minus that is the molar conductivity of the individual ions we represent by the minus z and minus u.

So, this is the molar conductivity of the individual ions and this is the molar conductivity of the electrolyte. Whenever talk we are talking about the molar conductivity of the electrolyte we are using the capital lambda. When we are talking about the ions we are using this smaller lambda.

So, if we look into these two expressions then what we can write these two expressions if you are looking into then the lambda capital lambda is nothing, but this is the expression which we have for the; for one type of ion. And this we expression we have for another type of ion. So, depending on the type of ion and number of positive ions which is generated we can rewrite that as this is the z lambda for the plus ion and this is for the lambda for the negative ions, just have a look at this expression.

So, what we have we can separate out this, this and F as for the positive ion this, this and this as the negative ion. So, what are we left with the nu plus and the nu minus.

So, this expression what we are getting capital lambda is nothing, but nu plus into the ionic mobility of the ionic conductivity of the positive ion, nu minus into the ionic mobility of the negative ions. This expression of molar conductivity, which you have is the sum of the individual independent contribution from each kind of ions present in the solution, and this is what is the Kohlrauschs law.

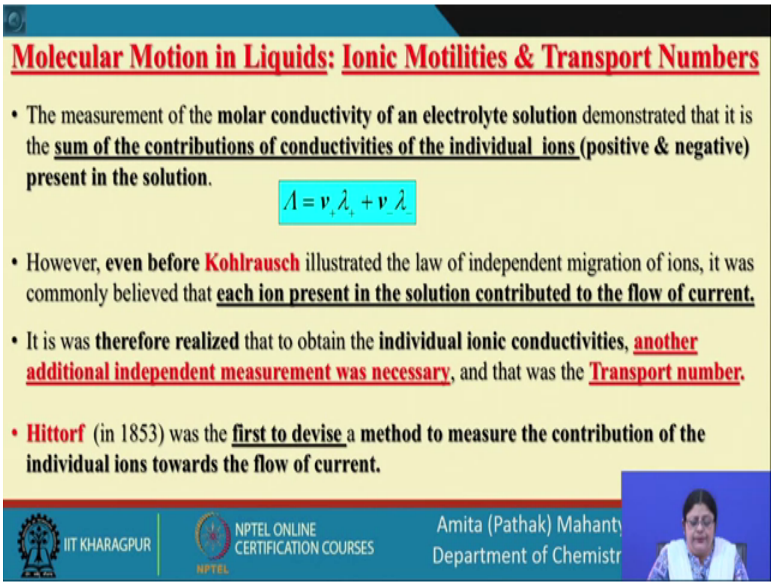
So, it is going to be correct or valid only if the electrolyte solution is infinitely dilute means it is in the limits of zero concentration. And since, the electrically charged ions will exert mutual in influence or interaction if they are present in large appreciable amount.

So, we have to consider the validity of the Kohlrauschs law only when inter ionic interactions or the mutual influence of one ion on the other is minimum or 0. And that is only going to be possible when we have in the limiting condition of zero concentration of the electrolyte.

So, under zero conditions under the conditions of approaching zero concentration of the electrolyte then this expression can be rewritten as lambda naught. The molar conductivity of the electrolyte is nothing, but the lambda naught contribution for the positive ion and the lambda naught contribution of the negative ion.

These are molar conductance of the cation and the molar conductance of the anion.

(Refer Slide Time: 15:45)



So, the from here we have the measurement of molar conductivity of a electrolyte; can be demonstrated to be the sum of the contribution of the conductivities of the individual ion the positive and negative ions in present in the solution. Again even before Kohlrauschs illustrated this independent migration of ions it was common to commonly believed that each ion present in the solution contribute to the total current that is flowing.

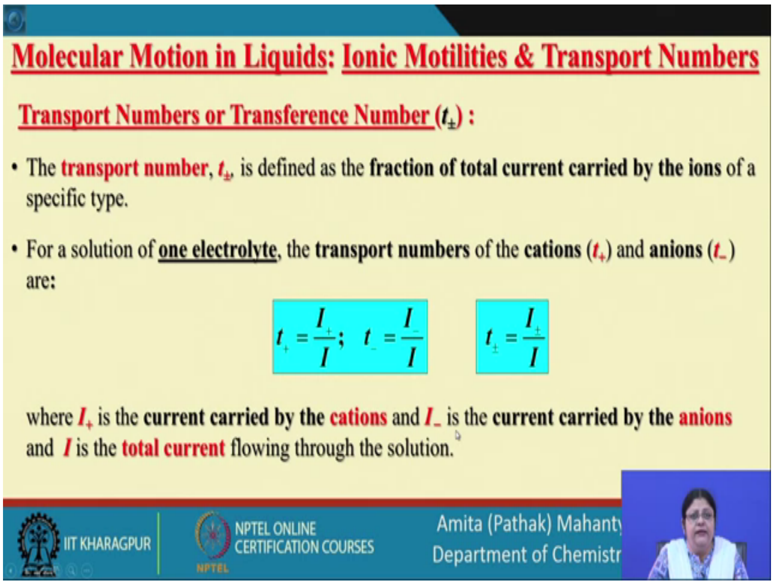
So, what we have here this is from whatever the Kohlrauschs law is from Kohlrauschs law have we have the contributions of the molar conductivity of the total electrolyte will be the sum of the contributions of the individual ion present in the solution.

And even before the Kohlrauschs law was established or demonstrated to have any independent the contributions of the each of the ions. It was believed that ions present in the solution contribute each of the ions present in the solution have some contribution towards the flow of the current.

Therefore, is it was realized that there must be another additional independent measurement, which was necessary to obtain the individual ionic conductivities. And that is known as the transport number Hittorf was the first he was a scientist. Who first in 1953 demonstrated or measured the contribution of individual ions towards the flow of current.

So, what we are now looking into we have trying to establish a relationship to find out how apart from the ionic the mobilities, apart from the individual ionic mobilities, what is the another parameter, which is necessary for which can contribute to the further information of the ions which are moving and that we now see as the transport number.

(Refer Slide Time: 17:58)



So, transport number is what it is? it is also times known as the transference number. We represent t plus minus; that means, we are talking about t plus as well as the t minus.

The transport number t plus minus is defined as the fraction of the total current carried by each of the ions of a specific type. Like if I say the t plus then I talked about the fraction of total current carried by the positive ions present in the system or solution system.

And if I talk about t minus then I talk about the fraction of current carried by the negative ions in the solution system.

So, suppose I have a solution of one electrolyte, it gets complicated if you have number of electrolytes, because each of the ions are going to contribute to the flow of the current.

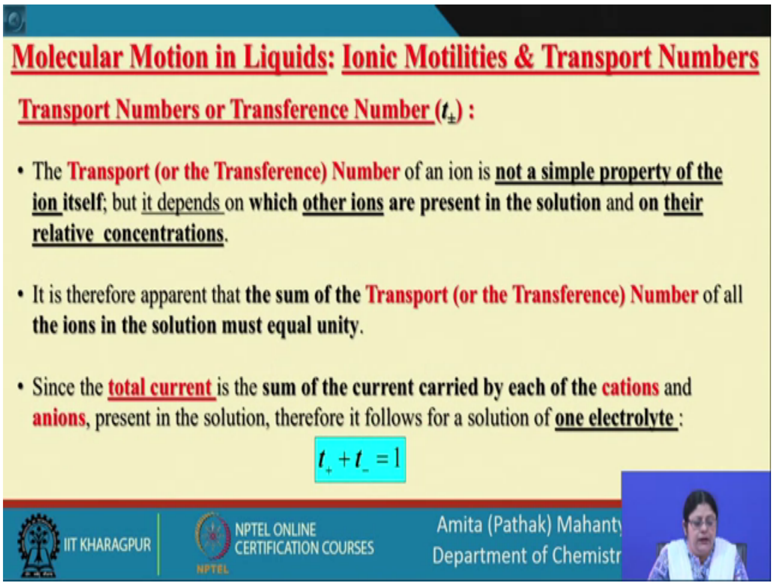
So, to be in the simplest form we take only one electrolyte. And one electrolyte we will have one type of cation and another type of anion only. So, only single type of cation and single type of anion will be present in the system.

So, for that situation the transport number or transference number of the positive ions can be defined as the ratio of the current carried by the positive ions divided by the total ion, the total current. Similarly if we want to find out the transport number of the anion present in the system that will be the ratio of that ion and the current carried by the anion divided by the total current that is flowing.

So, it is a fraction of the current which is carried by this negative ion, this is the fraction of the current, which is carried by the positive ion. So, when we represent this, which this can be further represent in the form in one form this t plus minus equal to I plus minus by t.

Here we are talking about taking both the anion and cation together and representing by one expression. This essentially means whenever we are writing plus minus t and plus minus I, this essentially means the t plus equal to I plus divided by I and t minus equal to I minus divided by I. This does not mean we are talking about it together; it is just representing that for both the ion type of ions, which are present in the system. So, I plus is the current carried by the cation and I minus is the current carried by the anion and I is the total current that is flowing through the solution.

(Refer Slide Time: 21:03)



Now the transport number or transference number of an ion is not just a simple property of the typical ion which is which we are looking into. It depends on the other types of ion present in the solution and also on the relative concentration of those ions in the solution.

So, it is a it becomes complicated, if we have number of ions present in the solution. So, we have simplified or we have avoided the complications by taking only one simple electrolyte system. Where we have only one solved which is giving rise to a positive charge and a negative charge of ions.

So, therefore, it is apparent the sum of the transport properties of all the ions in the solution must be equal to unity. That means, if I am talking about a electrolyte system, which is giving rise to one type of cation and only another type of anion.

That means, I am talking about a solution system, where I have only one electrolyte, then it becomes the total current which is going to be carried by the ions will be the individual contribution of the cation and the anion.

So, system becomes complicated, the system is going to get complicated the number of transport number definition gets complicated.; Because, if there are more than one type of ions present more than one type of cation or more than one type of anion present in the system.

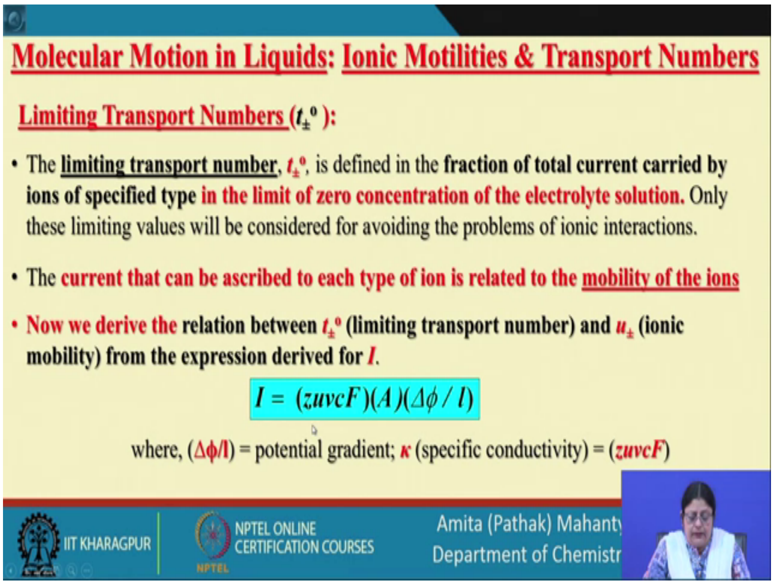
Because the contribution of the current is going to be carried by each ion present in the system, so, if I have different types of ion present in the solution, other than the one which we are looking into.

And the other types of ion which are present in the solution and their relative concentration will have a effect on the total the transport number of the ions of interest. To simplify what we have taken, we have taken only one type of electrolyte where we have one type of cations and only another one type of anion generated when in solution.

So, since each of the ions is carrying a fraction of the current. So, it is; apparent that the total current carried since it is a fraction, like; the total current if I say is 1, then the total fraction if I have positive ions carrying a part of the fraction and the negative ion carrying the part another part of the fraction. Then the total ion current which is carried should be the sum of the contributions of each of the ions which is present.

So, in other way other words we can say that total current is the sum of the current carried by each of the ions. The cations and anions present in the solution, therefore, for one type of electrolyte when solution we have this again the t plus and the t minus should be equal to 1. It makes sense because, these both are fractions and the fractions should add up to becoming 1 when the total current is considered right.

(Refer Slide Time: 24:37)



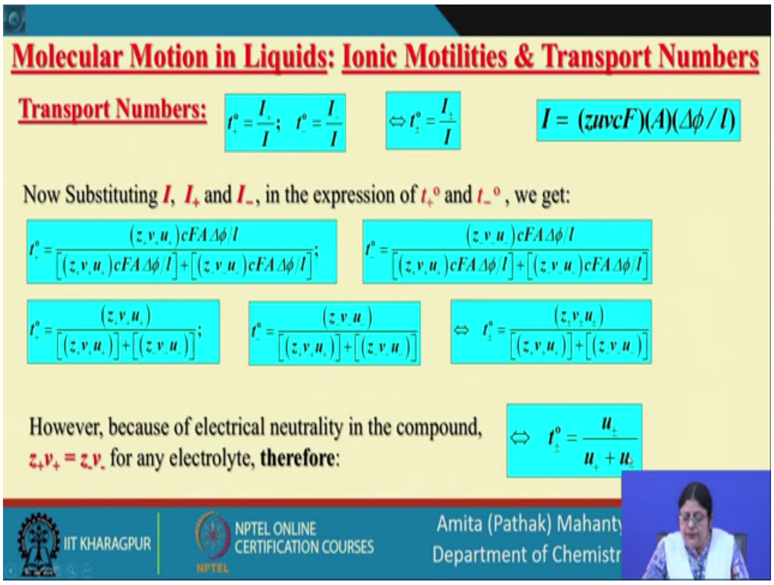
So, now we want to understand when we are talking about the transport number, what is the condition which we under which we can see the contributions of the each of the ions. Obviously, when we are talking about a limiting condition when we avoid the problems of interactions of ion is where we have the independent movement of the ions.

Is such a situation should be considered where we define the transport number or transference number? And this number now we can subscript it by superscripted by a naught, saying that it is a limiting transport number.

Limiting transport number is defined as the plus minus for each of the ions; the fraction of total current carried by the specific type of ion in the limits of zero concentration of the electrolyte, so, now we can derive a relationship between the transport number and the mobilities which we have derived previously.

And also from the expressions of I which we have, if you remember from the expression of I this is the I we have. This is the flux of charge into the area and this is the potential difference which we have previously derived. And this is going to be if the expression of I.

(Refer Slide Time: 26:11)



So, this is the expression of total I now if I want to find out what is the transport number under limiting condition? Then the I naught of the positive ion will be the contribution by the cation and by the total current which is present. And the for the negative ion it will be the charge now the current carried by the negative ion ok.

Now, the expression of current is we have written down here, now, to find out the fraction with what of the transport number under limiting condition. What we do? We substitute the values of I plus and I minus.

So, this you see you the I plus which we are going to be included in applying using the expression of I. We have derived before only thing is we are going to subscript it by the plus ion and minus ion.

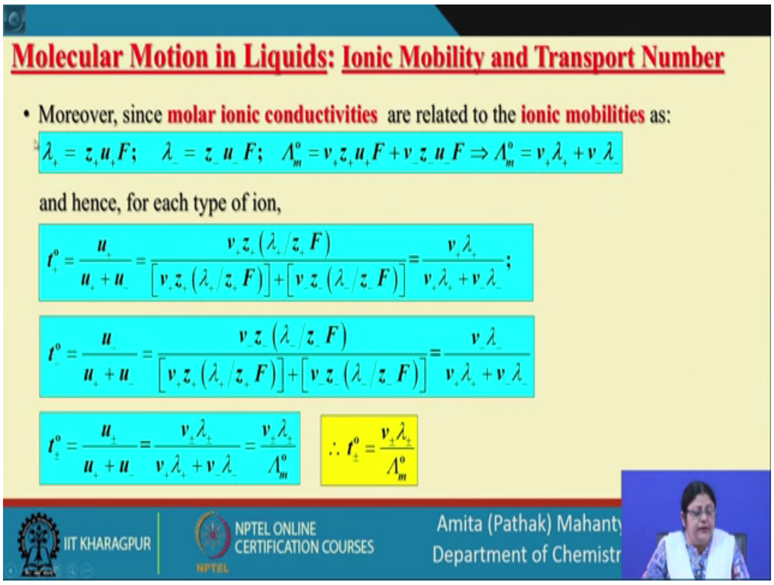
So, this is what we have, this is the plus ion, this is the number of formula units, then; which is going to be present for the positive ion per unit electrolyte electrolyte which we are using, and this is the mobility of the positive ion.

Similarly you have for the negative ion, if you take the ratios you seen everything is getting cancelled and eventually this is getting cancelled, this is going to get cancelled eventually you are going to get the down to a ratio of z u v of the negative ion. And z u v of the positive ion divided by the total z u v’s of the positive and the negative ion.

Now, since the solution is going to be electrically neutral. So, what happens the z and v of the positive should be equal to z v of the negative. So, if you can apply that what you have you can cancel the z u v paths, then you have the ratios of the mobilities.

So, you see we have derived the expression of the transport number of each type of ion and the limiting conditions of zero concentration of the electrolyte. In terms of the mobility of the each of the ions the positive ions divided by the mobilities of the positive and the negative ion.

(Refer Slide Time: 28:31)



Similarly and if you can if you remember the molar conductance of the one type of ion was z u F in terms of the plus ions and for the negative ions z u F in terms of the negative ions.

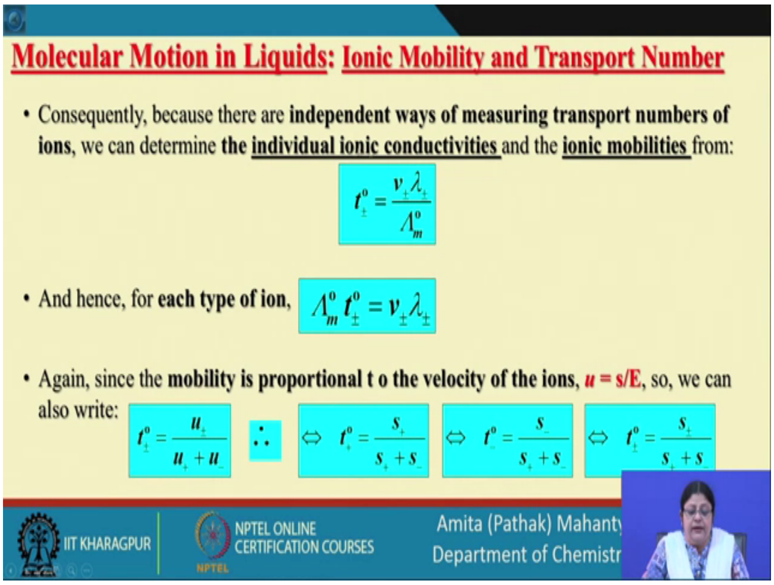
So, if you remember the under limiting conditions of; the electrolyte what we had? The molar conductance of the electrolyte was nothing, but this nu plus of the positive into the z u F of the positive ion plus nu minus of the negative ion and z u F of the negative ion.

This was again taken to be the z u z plus of the ions that means, this is the lambda and this is the lambda. So, we have u plus nu plus into lambda plus and u minus into lambda minus.

So, if I can replace this, I have in terms of the mobilities we have the expression of that transport number. Now in instead of the u if I replace that you can see u here is what, u here is lambda by z F for the positive ion. So, I have replace u in terms of the lambda divided by z u F ok. See this z and this z is going to cancel off so, what you are left with it is the nu into lambda plus divided by nu of the and lambda plus of the cation and the anion.

So, if you see what we have got? We have got that the transport number of the cation and anion in terms of the ionic mobilities. Now we have in terms of the molar ionic molar conductivities ok.

(Refer Slide Time: 30:35)



So, the independent because there are independent ways of measuring transport numbers; we can determine the individual ionic conductivities and mobilities from this expression.

That means, what we can say, the lambda naught for the electrolyte into the transport number of any type of ion will be the nu for that any type of ion into the ionic molar conductivity of that ion.

So, what we have? We have another expression which is possible. We have mobilities in terms of the speed, the drift speed of the molecules or ions which are moving in under the electric field; u will be to s by E. If you remember this expression which we had derived under the previous lectures.

If u equal to s by v then, this expression I replace the u in terms of s by E. E is the constant electric field which is applied so, E will going to is going to get cancelled. So, what we have? We have the E the transport number and the limiting condition in terms of the speed of the positive ion divided by the speed of the summation of the speed of the positive and the negative ion.

So, we can say that; transport number of the ion is nothing, but the ratio of the speed of the a particular type of ion divided by the speed of the cation and anion present in this system.

So, this is that various expressions which we have got to relate the transport numbers of a particular type of ions, with the ionic mobility, with the speed of the ions and in terms of the ionic conductivities.

Thank you so much.