Molecules in Motion
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Lecture – 24
Molecular Motion in Liquids (Contd.)

So, welcome to another lecture on Molecules in Motion. Last class if you remember we had introduced the concept of transport numbers or transference number; and we had talked about how transport number can be obtained by various means. Whatever expressions we had derived so far in terms of the mobility, in terms of the molar conductivity, in terms of the molar the ionic speed we could relate each of these parameters with the transport number or transference number.

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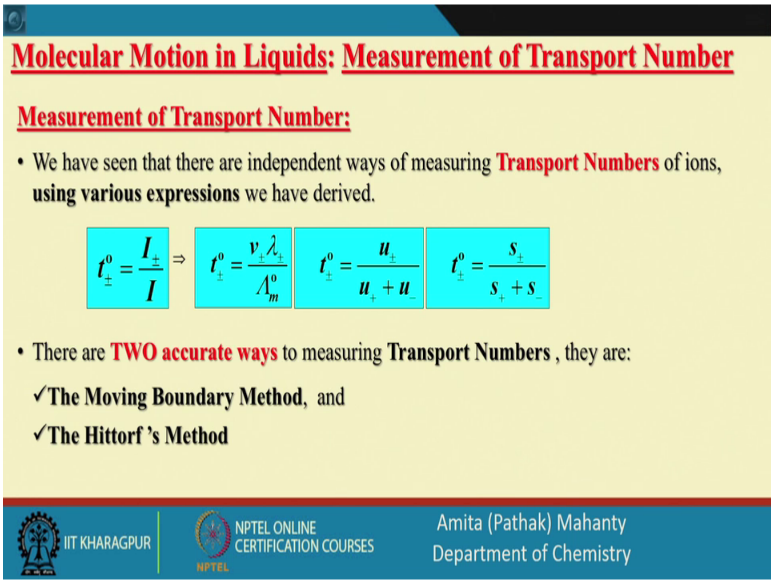

Transference number what we have described was the ratio of the fraction of; it was a fraction, it is a ratio of the current carried by the one type of ions which is positive or negative divided by the total current which is carried through the electrolyte system. So, the various expressions which we had derived in the last class was: this is the definition of the transport number, when I have plus minus I individually mean that contribution of the plus ion and the negative ion. When I say this is naught; that means, I am finding out the transport number under limiting conditions of 0 concentration of the electrolyte.

So, if I have this definition from this definition what we derived in the last class, was the various expressions of the transport number or transference number in terms of the molar ionic conductivity, the ionic mobility, and the ionic speed.

So, this is if you remember this is the transport number for a any type of positive or negative ion. Remember we had talked about the condition where we have only one type of electrolyte not a mixture of electrolyte; one type of electrolyte giving only one type of cation and one type of anion ok.

And from that expression we had derived the expression for how that can be related to the ionic conductivities of the each of the ions. And this was the molar conductivity of the electrolyte at infinite dilution. This was the ratio which we had seen for the positive and the negative ion.

Similarly the ionic mobility of the ions individual ion plus and minus divided by the total ionic mobility of the plus minus ions in the solution. Similarly the ionic mobility of either plus or the negative ions is going to be equal to the speed of the ions at infinite dilution obviously, when we have the total the speed of the positive ion divided by the speed of the positive and the negative ion in the system.

So, this plus minus represents we can expand this to either positive charge or to the negative charge; denominator always is always the summation of the two ions which whatever the property may be either it is ionic mobility or the speed or the molar conductivity of the electrolyte.

So, the now we have also talked that this is these parameters are measurable parameters. So, we can if we want to find out say the ionic mobility or ionic conductivity or ionic mobility of the ions. We can do that if we have the knowledge of the transference number at infinite dilution of the solution. We have taken infinite dilution of the solutions so as to avoid the inter ionic interactions between the ion which complicates any relationship which we have derived so far.

So, there are two types of method to measure the transport property and the two most famous accurate methods are one is the Moving Boundary Method and the other one is the Hittorf's Method. We are going to discuss each of the measurement methods of transport numbers or transference numbers.

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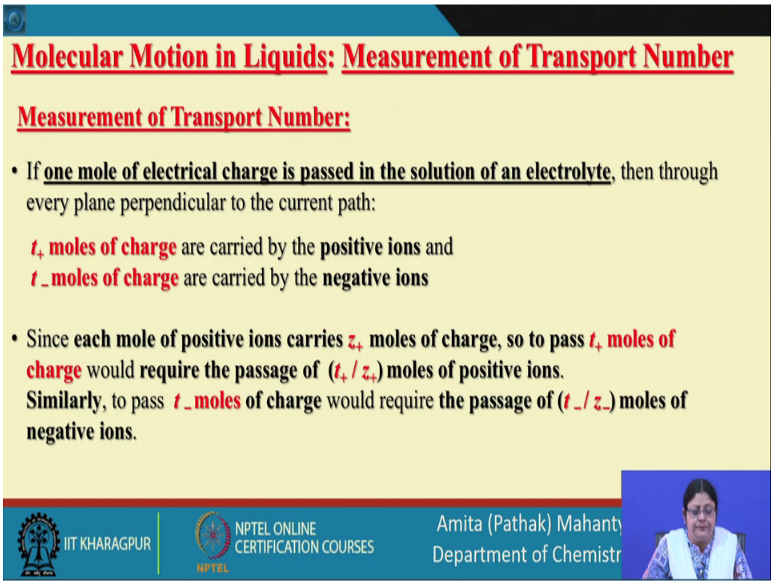

Now, before doing that what we need to understand if I have one mole of the electrical charge, is passed through the solution of a electrolyte. Then through every plane that is perpendicular to the current path you have t plus moles of charge are carried by the positive ions and t minus moles of the charge carried by the negative ions am I clear.

What I am trying to say if there is one mole of electric charge passed through a solution one mole of electric charge is passed through the solution, and the solution is composed of one type of electrolyte giving rise to one type of anion and only one type of cation. Then through if one mole of the charge electric charge is passed through the solution then, through every plane that is perpendicular to the path of the current we have t plus moles of charge carried by the positive ion and t minus number of moles of the charge carried by the negative ion. What is the t? T is the transport number of the positive ion and t minus is then transport number of the negative ion ok so each mole of a positive charge.

Suppose we have z plus as the charge of positive charge mole if each mole of a positive charge z plus and to pass t plus moles of charge would require how much we will require the passage of t plus divided by z minus moles of positive ion. Is that clear?

What we are trying to come to? The each mole of the positive ions suppose it carries a if positive each positive charge is represented by z plus moles. So, each mole of positive ion if it passes if I say t plus moles of charge would be past, then the that would require t plus by z plus moles of the positive ions. Similarly to pass t minus moles of charge would required the passage of t minus divided by z minus moles of the negative ions. Where t plus is the transport number of the positive ion and t minus is the transport number of the negative ion.

So, I hope which is this is cleared each mole of the positive ion carries z plus moles of charge. So, to pass z plus moles of the charge would require the passage of z plus by z, t plus by z plus moles of the positive ion and t minus by t z moles of the negative ion. So, this will be more clearer when we talk about the Hittorf's method.

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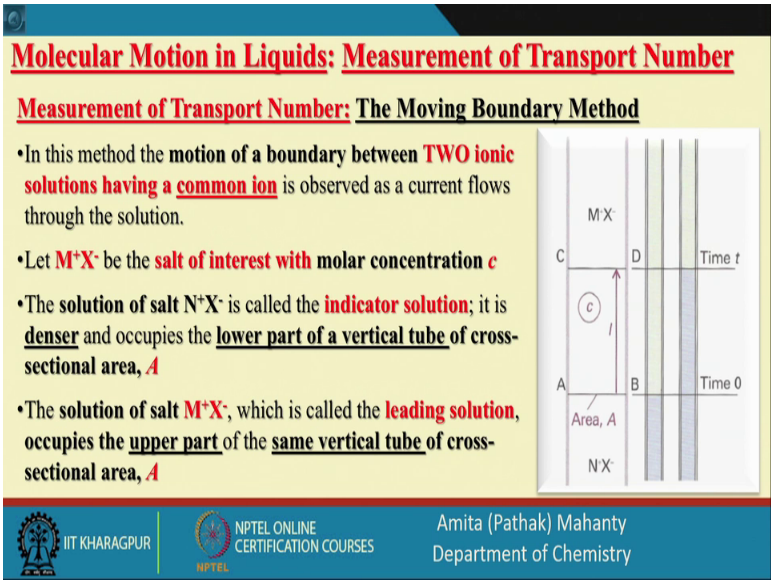

Now, let us first look into the Moving Boundary Method as the name suggests the in this method the motion of the boundary of two ionic solutions have a common ion is observed as the current flows through the solution. So, what we have we have two ionic solutions where one ion is going to be common either the cation or the anion when we are trying to find out the transport number of a cation then we usually take the anion to be as the common ion ok.

So, if I have a salt which is of interest says M plus z minus X minus of molar concentration c ok. If I have we want to find out the transport number of the ion M plus and the salt which we are taking is M plus x minus has the concentration molar concentration of c ok.

Now, see what we have saying we have a the method when motion of the boundaries of two electrolyte two ionic solutions are into consideration, when we have a flow of current through the solution. And here we have taken the common ion to be a N ion and the two cations are M plus.

We can represent them as the one which is of interest for which we want to find out the transport number another solution which is which is another ionic solution is the plus ok. So, we have two solutions two electrolyte solutions that have one common anion that is z that is X ok.

So, two ionic solutions or the salts are this is one and let us, N X be the other NX is one and NX is the other. What we are going to see? We are going to see the motion of the boundaries between the two ionic solutions with that we have. And these two ionic solutions which we are which we are having is one is MX and one is NX which is of interest for which we want to find out the transport number let that be N now the condition is that we have a common ion.

Since, we are interested in finding out the transport number of that positive ion. So, let us keep what we have kept the anion as the common. So, X is the common ion between the two salt solutions which we have MX and NX and MX is the one of our interest and that is of concentration molar concentration c ok.

Now the solution of the NX is called the indicator solution, it is of denser it is density is going to be higher and if I have a tube like this I have MX here I have NX here. And I have the boundaries demarcating this is we are saying this is at the zeros condition and zero condition I have at this position where I have only the NX and here I have the MX ok. So, the lower portion of the vertical tube which cross section area a will contain the NX and that is going to be the indicator solution and indicator solution will have a higher density compared to that of the lead solution which is of MX ok.

And this ion is of our interest MX the M ion is what for which we are finding out the transport number. We are finding out the transport number of the M ion. So, what we are look looking into we are trying to find out the transport number t and t plus, and this t plus is corresponding to the transference or transport number of the M cation which we have in the solution system.

So, the solution of the salt MX which is the lead solution occupies the upper portion of the vertical tube of the same cross section area. So, what we have this as the common area which we will be looking into.

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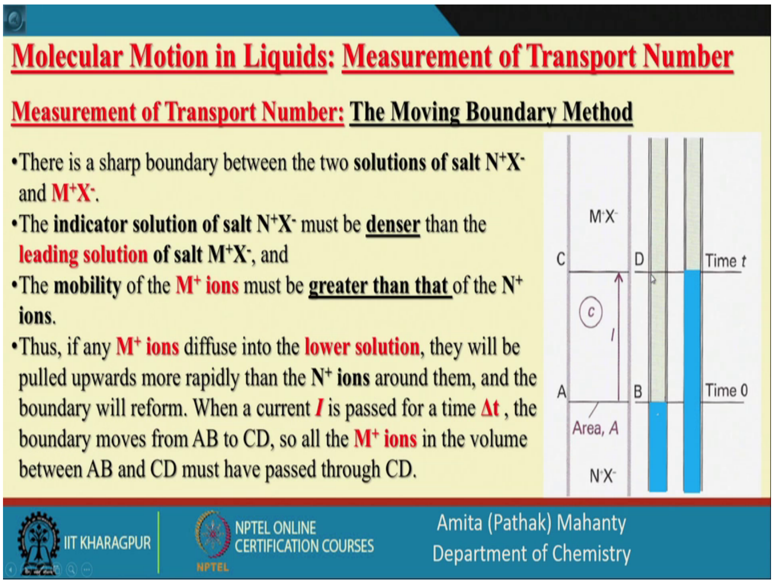

So, there should be a sharp boundary between the two liquids N X plus M X. The indicator solution the indicator solution is this that is N X is denser than the lead solution lead solution is the M X. And one more thing needs to be kept in mind that the mobility of the ion of interest should be greater than that of the indicator of the cation present in the indicator solution ok.

So, the indicator solution the cation is N and the lead solution and of our interest for which we are looking into the transport number is M. The mobility of M should be greater than that of the N. So, what is the criteria that the MX solution which is the lead solution which will be in the lower part of the tube should have a higher density compared to that of the leading solution of MX; where MX, M is the ion of interest for which we are trying to find out the transport number. And of these the M ion is supposed to have a greater mobility than that of the N ion in the solution ok. If M ion what will happen is if M ion diffuses into the lower solution. They can be easily pulled off very rapidly the compared to that of the N ions around them and form a sharp boundary we form the boundary again.

So, suppose I have a current I passing through the solution this is the column which I have if at delta time t the boundary moves from A to CD. So, what is our interest in the volume our volume of interest is AB CD, this is the volume of interest ok. So, what happens the MX is going to diffuse into the solution and then what happens is the as we move from AB to C CD the whole volume. Then what happens M a plus ions the M plus ions in if it comes into the volume elements; that means, it has crossed this boundary CD ok.

So, what we have next what we are going to monitor. We are going to monitor when we are passing a current of I in delta time in time delta t then, when the boundaries this bound this is going to move into this. That means, it is crossing the CD boundary we are looking into the number of ions which will be present in this volume ABCD ok.

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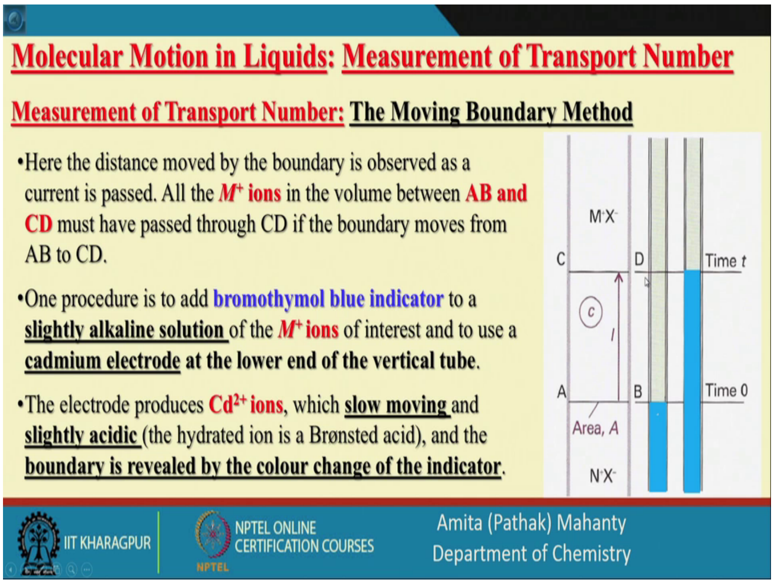

So, the distance moved by the boundary is observed as the current is passed ok.

All the M a plus ions in the volume element which is ABCD must have passed through the CD barrier to move into this zone ok. What is usually done, One of the procedures is you use bromothymole blue indicator to the slightly alkaline solution of the M a, M a plus ion of interest to use and use a cadmium electrode at the lower end of the vertical tube.

So, we have a cadmium electrode in the lower end and we have added bromothymol blue, indicator into a alkaline solution of the of this now the electrode which we have placed in the bottom is a cadmium electrode and the cadmium electrode will produce a cadmium plus 2 ions which will which are slow moving and they are slightly acidic.

So, I have the alkaline solution where you have the indicator mixed into the salt solution of MX and what happens the cadmium ions generated from the cadmium electrode moves slowly and these are acidic.

Slow moving ions and when they move and they when they come in contact with the M a plus ion which is having the indicator thermolye bromothymol blue they will have a colour change. So, this will be indicated in as a colour change when we see the boundaries.

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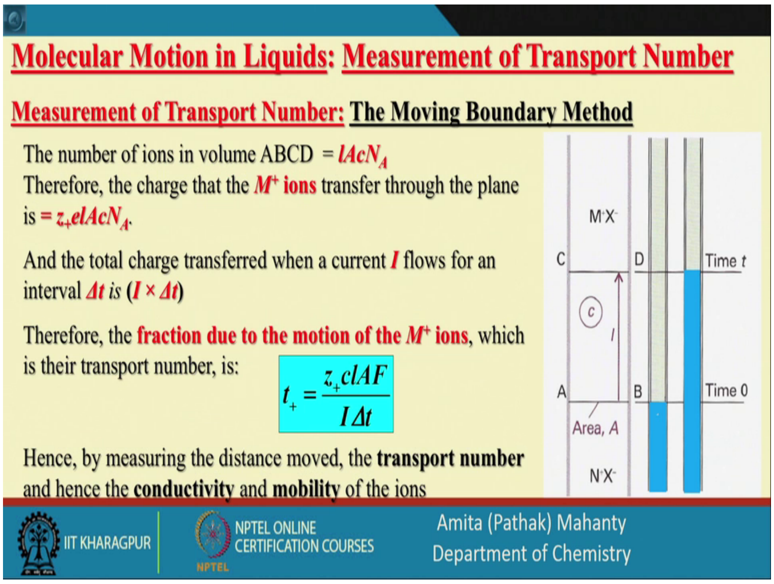

What we have looking into now? We are looking into this zone, this is the zone which we have in which you have what will be the concentration of the number of ions of MA which is going to be present here? The total number of ions which is going to be present here will be the concentration of the ion electrolyte, will be the concentration of the plus ions of the solution into the total number of at would into the Avogadro number.

The concentration into the Avogadro number will give you the total number of ions in the volume element. This is that l and this is if the cross section area is a then the volume element is going to be l into A. So, the total number of ions in this will be l into A into the molar concentration into Avogadro number. That is what we have total concentration of the electrolyte is equivalent to the total number of ions which is going to generate. So, this is going to be concentration of the electrolyte into the Avogadro number. This is the volume element ok.

Therefore, the charge that MA plus ion it transfers through the plane is going to be, now we are looking into the charge which is going to be transferred. It is going to be a positive charge z plus into how much that will be e z e is going to be the charge ok.

So, z e into the total number of ions present in the solution that will be the charge associated with the M plus ions and z should be positive because we are looking into the positive ions. So, the charge which is going to be transferred to through this plane of passing through CD to coming into ABCD volume will be nothing, but z e. Where z is the positive charge, into the area, into the l, which is the volume into the total number of ions that is molar concentration into Avogadro number.

Now, what is the total a charge which is transferred the total charge this is transferred when you have a current I flowing for a interval delta t is equal to I into delta t ok. The total current which is flowing through the system is I and if it in the interval is delta t. Then the total charge which is going to be transferred is going to be I into delta t ok.

So, the fraction of the motion of the M plus ion can be given by the total number of the and the charge which is carried by the z e type of ions, divided by the total charge which is transferred when the I current flows at delta t time. So, this is going to give you the charge for the flow of i current through a integral of delta t right.

So, this is the total charge which is getting passing at del time delta t and this is the total charge of the charge of interest which is contained in the volume element, ABCD and think there is a simplification here you have e into Avogadro number equal to F. So, we have replaced e into Avogadro number as the Faraday constant into the l into a is the area and c is the concentration of the electrolyte. So, if we know the concentration of the electrolyte which is going to give rise to the, lead solution which is the cation of our interest for which we are finding out the transport number.

So, we are this is the charge carried by the ions which is passing the border CD coming into this, diffusing into this solution to generate after time t. This is the region which we have this is the region where you have the ions of interest M a plus.

So, the total number of ions charges charged species in the volume element is going to be z e into Avogadro number into c into l into a; z if I multiply e with the with the Avogadro number I get the Faraday constant. So, this is the total number of charges in the volume element and this is the total charge. We due to the flow of current I at delta time t.

So, this is the total charge which is associated and this is the total charge carried by the ion positive charged ion M. So, this fraction gives you the, transference number of the M a plus ion. So, if I know the transport number of the M a plus ion, then I can find out the transport number of the z in the x ion that will be if this t plus and t because t plus and addition of t plus and t minus should be equal to one.

So, if I have t plus known then I can find out the t minus because, one minus t plus should give you the t minus. So, if we know the transport number of the positive charge. We can find out the transport number of the negative charge in of interest here it will be the x.

So, similarly we can do another experiment, where you have the cations common and anions different and do the movement of the charge cross to applied field and see what will be the t minus. And hence if you either of the t transport numbers are found you can find out the respective other, if I know the t plus I can find 1 the t minus by 1 minus t plus will be giving you t minus.

Similarly if we do the experiment instead of having a solution where you have a anion common, if I say take a cation common that time I can find out the transport number of the anion. So, here we have sorry if here we have the anion common. So, we found out the transport number of the cation.

So, similarly if I want to find out the anion I have to keep the transport number of the cation common ok. So, if we have if we know the z t plus then I can find out the t minus and since we can you know the transport number. We can hence calculate if you see the expressions from the previous expressions. Since, you have t plus calculated then you can respectively find out the values of mobility, you can find out the values of the ionic conductivity and also the speed of the ions associated with each type of ion in the solution system.

So, this is what the Moving Boundary Method is. In the next class we will take up, what the Hittorf's method, and how we use the Hittorf's method to find out the type of transference number associated with the electrolyte of interest.

Thank you so much.