Molecules in Motion
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Lecture – 21
Molecular Motion in Liquids (Contd.)

Welcome to the 21st lecture on Molecules in Motion. We were discussing about ionic mobility and how they evolve it can be related to the ionic conductivity. We had talked about the various parameters which affect them and we had talked about the values of the ionic conductivity and mole the molar conductivity values which we are we can relate to.

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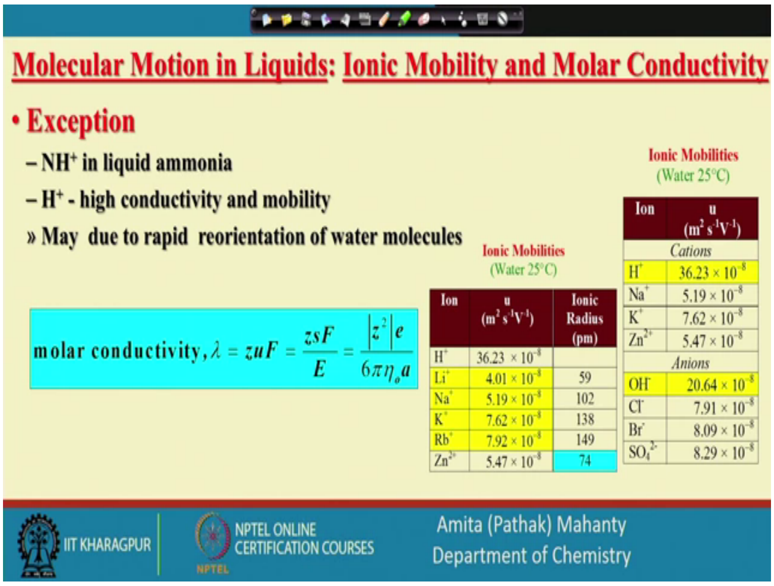

So, what we had last talked about was the anomalies which are usually observed. If you see the hydrogen and OH minus ion the hydroxyl and the hydronium ion, you will see if you can notice the values of H plus and OH minus are extremely at least. If you any standard values if you can talk about it is almost 50 times, then any values of. Usually, it is any cation will have the usually the molar conductivity is in range of say 40 to 80, but here you get much higher. So, what is the reason is when we are talking about H plus ion and OH minus ion are they so different.

Whenever we are talking about transport of charge by ion, what we talk about? We talk about the ion moving through the medium along with the solvated the ions are actually solvated. So, along with the sheet of the solvent molecules they roll through the medium when they are moving from one end of to another when a charged particle is moving under electric field in a solvent medium they are actually a cation or anion has a sheet of the water or the solvent molecules on its surface and it is rolling through the medium.

What we have and here we had seen that a here, if it small does not necessarily mean that you have a higher mobility or higher conductivity. This is actually if we are talking about water medium particularly wherever in whichever medium the ions are getting more solvated and water is one of the medium where you have high polarity. So, it is one of the solvents which you have the ions greatly solvated or you have an interaction of the charged particle along with the dipole of the water molecule.

So, here what we are looking into if the sizes of hydrogen atom is just one proton. So, you can think of one proton being the smallest of size. If this is the smallest of size, then what we had talked about the smallest of charge size will have a high charge density over it. So, they will have the highest solvated radius that is the hydrodynamic radius. So, if they have the highest hydrodynamic radius then this should value should be less. So, should be this, but we do not see that happening when we are talking about H plus and OH minus what is the paradox.

The same thing has been noted when we are having the NH plus in a liquid ammonia system liquid ammonia is also a very good solvent medium. So, what happens when we have these two systems or OH minus in the system? Let us look into it.

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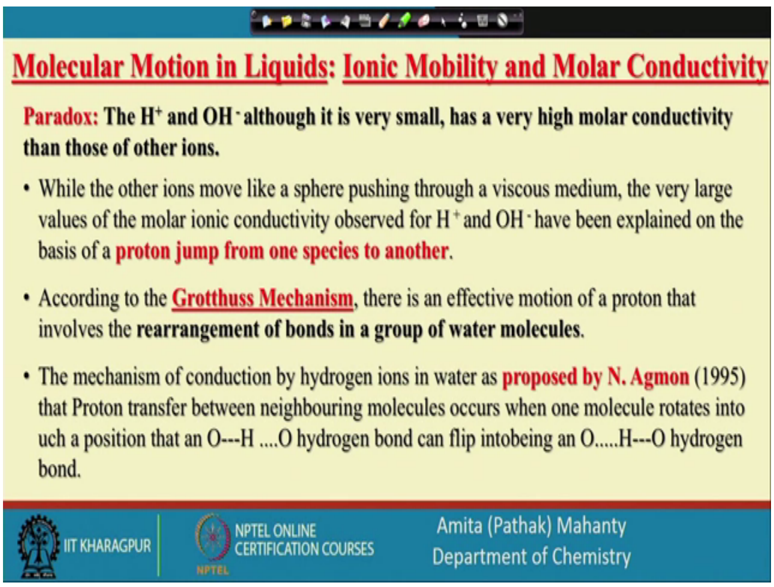

The OH plus OH minus and H plus although they are very small, they should have very high charge density on surface. And if they have very high charge density, they should have a very large solvated radius, but they do not and its and that should give rise to a lower value of ionic mobility or molar conductivity, but that is not what we observe the H plus and OH minus ion.

Although very small, have very high molar conductivity and ionic mobility compared to the other ions. What happens is while the other ions are moving through the viscous medium wrapped around in the sheet of the solvated molecule whatever the solvent may system may be. And very these ions are moving through rolling movement through the viscous medium and the very large value of the molar conductivity observed for H plus and OH minus is because they just do not they are not assuming the movement of rolling through the media or viscous medium.

But it can be explained on the basis of the proton jump phenomena from one species to another. So, what happens? While the other ions move likes spheres pushing through a viscous medium? Very high large values of molar conductivity observed for the OH and H plus ion is not through that similar kind of movement of the ions through the medium, not through rolling movement, but through a hop jump mechanism and where you have the proton jump from one species to another.

This is known as the Grotthuss mechanism; this is Grotthuss give us this observation. There is an effective motion of the proton that involves the rearrangement of the bonds in a group of water molecules ok. The mechanism of conduction by hydrogen ion in water was again proposed in 1995 by Agmon that the proton transfer between the neighboring molecules occur when one molecule rotates in such a position that the OH of the hydrogen can have flip into being something like this, hydrogen bond.

So, what we are talking about? We are talking about a proton transfer between neighboring atoms occurs when one molecule rotates into such a position that a bond of O and H; the hydrogen bond can flip into being O and HO. You see the position of the hydrogen bond is different. I have diagrams to show you that.

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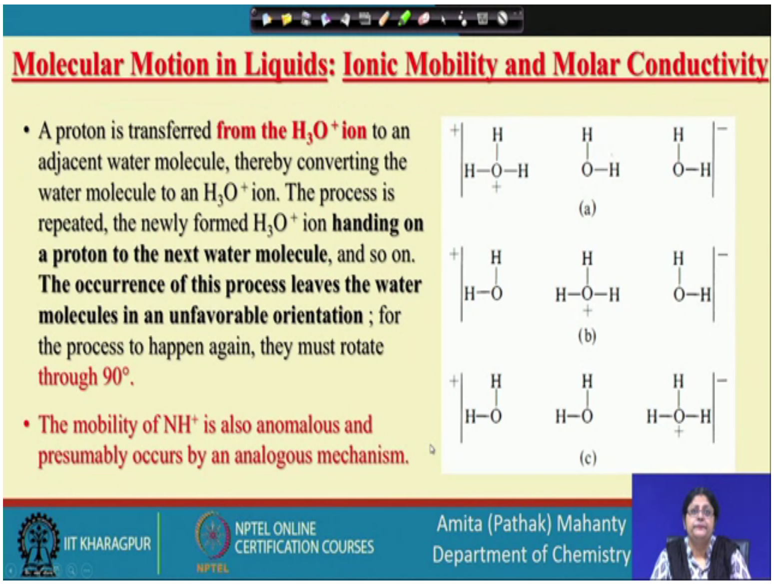

This is how the diagram can be looked into. The proton is transferred from one hydronium ion to the adjusting water molecule. See this is the water molecule this is not hydronium, you have that solution system applied against the electric field.

So, what happens? The proton is transferred from this hydronium ion to the adjacent water molecule and thereby converting the water into a hydronium ion. So, as soon as the proton is getting transferred here this is going to become a hydronium ion. This plot process is repeated, the newly formed a hydronium ion will now transfer its proton to the neighboring water molecule and so on. It will keep going on that way.

This occurrence of this process leaves the water molecules in an unfavorable orientation ok. So, in this if you see this is the first position which you have just have a look at what happens. This is the second proposition which you have ok, second the hydrogen ion proton is transferred to this. So, this becomes a protonium ion and the next this is going to be transferred to the neighboring one. So, this becomes a protonium ion ok. But when they are transferring this proton what happens, the in the process the molecules becomes unfavorably oriented.

So, if this unfavorably oriented; there are a number of hypothesis now it the exact mechanism is still not very available in general textbooks. But whatever we have understanding based on that is what we are going to talk about it is that it is a proton of one hydronium ion being transferred to the neighboring water at molecule. So, that this water molecule becomes hydronium ion and this again you have a hand to hand to sort of transfer of the proton from the system one system one molecule to the other.

So, what you see here? It is the hop jump of the proton from one molecule to the other. Here we do not have the water molecule surrounded by a solvated other water molecules and becoming a sphere sort of a thing and moving in the viscous medium.

So, it is only the transfer of transport of the proton from one molecule to the other protanium ion. If they is first generated and that proton gets transferred to the neighboring water molecule. Only thing is the molecule has to went to regenerate again to do the transfer the molecule has to reorient favorably and to this reorient favorably they have to have a flip of 90 degree.

So, this is how it is supposed to be occurring and that is what we take it how the conduction is happening for H plus ion. The mobility of an H plus is also analogous to whatever mechanism which we are discussing for the hydronium ion.

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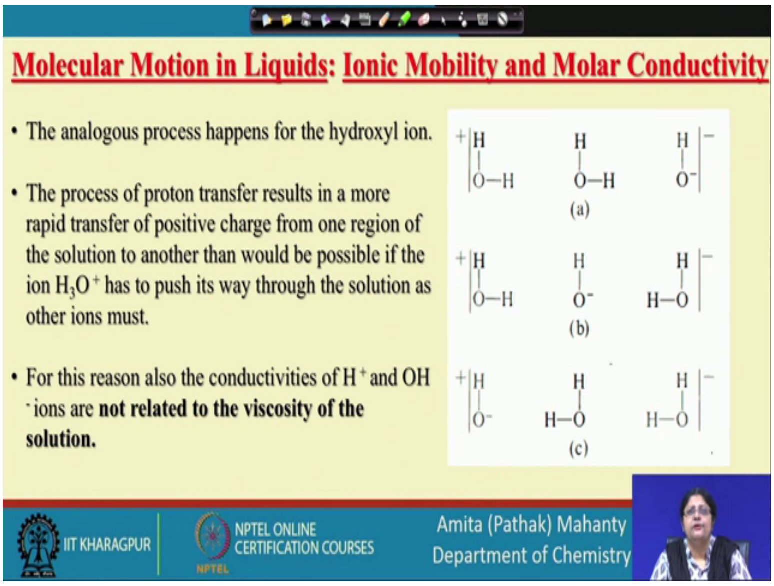

Now, if you see the hydroxyl ion also has a similar parameter if you have a look at the values of the molar conductivities, you will see that though hydronium ion has a lower value compared to hydrogen in terms of the mobility. But they are in terms of the other anions which you have compared to that it is much higher; it is a order difference. So, what you have? We have a similar system for the transfer of charge for hydroxyl ion.

The process of proton transfer results in more rapid transfer of positive charge from one region to the other. The solution of the solution and then it is possible if the hydronium had to hydronium had to push through the solution. Since it is not pushing and rolling through the medium. So, it is only through the proton jump process which we have. So, if it is you have a look at here how this is this is the first position how the H minus O minus charges are getting transferred you have it here first negatives electrode it is going to be having 1 O minus here and that it is getting transferred. It is not a proto it is a negative, it is a whole movements sort of a situation. It is not that it is actually the negative ion is moving it is the opposite of a proton transfer which is actually occurring.

So, what we are looking into? We are not looking into the molecules having a solvated layer pushing itself across the solvent medium. It is just through the transfer of charge from one molecule to the other is how the charge proton charge is getting transported from one end to other. That is the reason they are so high in their mobility values or conductivity values.

Since they are not moving through the solvent medium, despite the expression having the expression for ionic mobility as well as the expression for the molar conductivity, they have inversely proportional to the viscosity coefficient of the medium. These two terms are inversely proportional to the viscosity of the medium, but since the molecules what were the charges which we are looking into H plus and OH minus. When they are moving through these ion are moving through the medium, they are not rolling through this medium, but their just a proton transfer from hop from one molecule to the other.

So, what you have? These their mobilities or their conductivities is not going to be related to the viscosity of the medium right, it makes sense.

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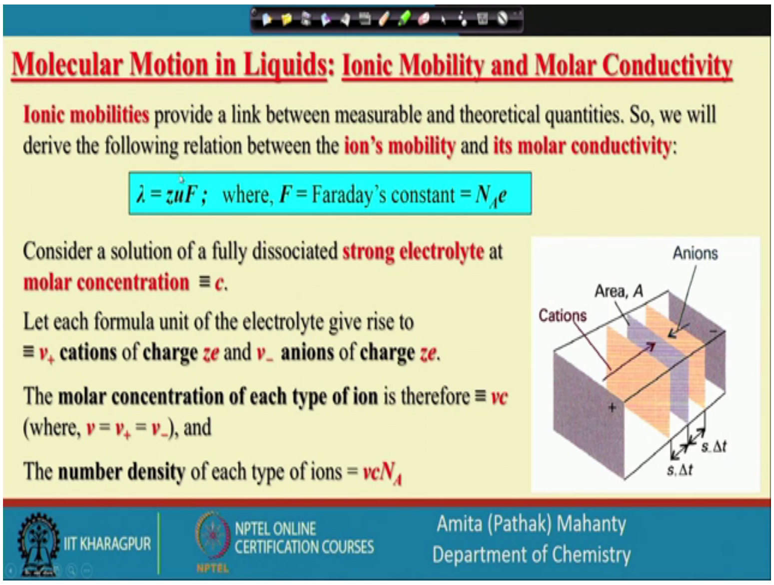

Now I will go into the actually the derivation of when we talked about how molar conductivity can be related to the ionic mobility, is this is the expression which we had taken in the last class as given and I had told you that we will be deriving this expression.

So, actually what happens? Ionic mobility is a very important term because it can it is a link between measurable parameters to that that of the theoretical quantities which we have. See we can if we have ionic mobility, we can relate to the conductivities and we can eventually if talk about other parameters when we talk about say transference number and other things when we have the charge transferred by a particular ion. We measure how to find out the how much charge is transferred.

So, these things if we want to go into we need to know the exact relationship, we have between the ionic mobilities and the conductivity. For that this concept what we are going to deal with is something which we have dealt when we were talking about the transport of in the gas phase gas medium. When we are talking about movement of gas through a distance where you have a velocity associated with the gas particles.

So, what we have talking about? If we say and we take a electrolyte which is a strong electrolyte completely dissociated into the respective ions. If the molar concentration we see of the particular electrolyte you are taking and suppose they gave rise to say nu plus a cation of charge ze and nu minus cation of z against ze.

If the molar concentration of each type of ion is such that if you see this is comes from the formula unit. So, I am if I say that the positive formula unit parameter and the negative formula unit parameters are equal, then we can say the molar concentration and we assume that it is equal and represented by a generic term nu.

Then that molar concentration of each type of ion which is there in the system, it can be nu plus it can be nu minus both should be equal because you have actually eventually dealing with the neutral solution. So, what we have? We have c is the concentration of the electrolyte which we have. So, what will be the concentration of each of the ions?.

If c is the concentration, c into the number of the formula unit should be multiplied by for cation as well as anion to give you the and since they are both equal we just say nu c, but you have to remember whenever we are talking about a electrolyte we are taking the contribution of the positive and the negative ion in this solution.

So, if this is the concentration of the ions, this c is in moles per liter; this is in moles per liter now I want to find out I have already say this is the moles molar concentration of ions. The total number of formula units into the concentration of the electrolyte gives you the concentration of the each type of ion we are dealing with.

Now, what should be the number density? The number of particles in the volume of the sample. How do you find that out? This is the moles per liter; 1 mole it is going to get you has Avogadro number of particles. So, you can multiply by Avogadro number to give you the number density. So, the number density is the molar concentration of the ions that is nu into the concentration of the electrolyte c into the Avogadro number ok.

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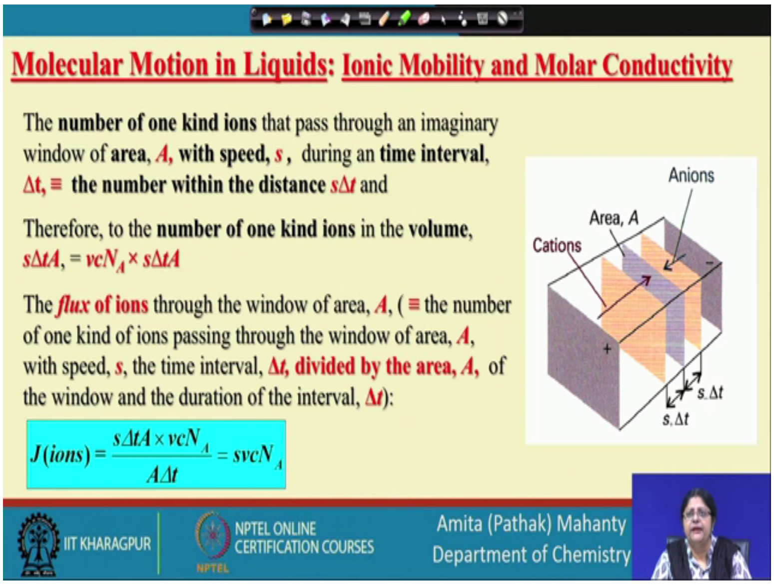

Now, suppose the number of one kind of ion let it be plus or minus passes through imaginary window, let have a look at this. We are starting from here; this is the place we are starting. We can go either this way or this way ok. So, and the if you are having the cations, then it is you are moving this towards this and if you are having anions you are moving this side; this is the negative electrode this is the positive electrode.

So, cations will be moving towards the negative electrode and ions will be moving towards the positive electrode. So, we are not going to be now associating whether it is a plus charge moving or the minus charge moving. We are taking that whatever per plus charge is there in the solution equal number of minus charges are there for the associated ions because eventually we have to have an electrically neutral system.

So, the number of any kind of ion when it passes through imaginary area A and suppose they are moving with the drift speed s, during a time interval delta t, then what is the number of the particles within that distance? So, that number of particles that is passing through this window, number of particles that is passing through this window that particle moving with the velocity s and in time interval delta t gives you the number of particles within the distance d; that d is nothing but from Newton’s law you have the speed into time speed equal to distance by time. So, the distance is equal to speed into time.

So, this is the length of the distance in which we are having a kind of one type of ion passing through, the area A which is the window. So, if area is this area is through which the sink is passing, this orange one is the area through which it is passing towards this say magenta color. So, this is the place when we are looking into. So, this is the distance you have and this is the total area you have.

So, whatever is contained in this zone, in this volume what will be the total number of ions in this volume? We know that the total volume will be the distance s whatever plus or minus into delta t into the area that gives you the volume which volume element which we are interested in and what is the concentration which we have said, the ionic a number of ions present is going to be the number density; which is nothing but we see into the Avogadro number.

Now, we have talked about flux in previous classes. Flux of ions, what do you mean by that? Flux of ions that is passing through this orange window whether from this side or from this side? The flux of ion passing through the window A is the number of ions of one kind passing through the window of area A with the speed s in time interval of delta t divided by area divided by the time duration.

So, the flux is defined as the total number of particles passing through the window of interest of area certain area moving with a certain speed at in certain time interval will be equal to this will should be divided by area and the delta t, the time interval that gives you the flux of ion present in the unit volume that is this volume right.

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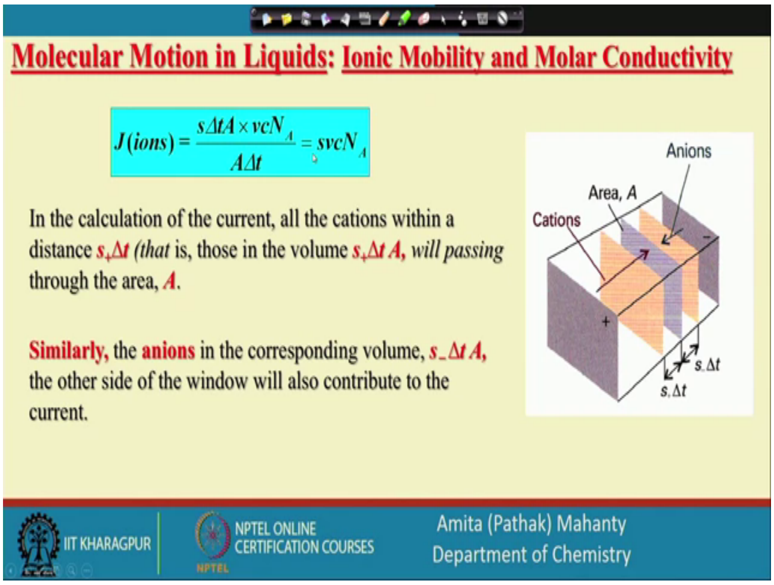

Now, so, now, we have this expression; this is the expression which we have, A gets canceled off. So, what we are left with? We are left with the expression of the flux of iron being this is the drift speed into the formula unit which we are getting this is the concentration of the molar concentration this is the Avogadro number.

Now, in the calculation of current all the cations within say this distance those with within the volume this pass through the area this. Similarly, if you want to look into the anion then correspondingly the ions moving with the velocity subscript as minus s minus; the velocity is not minus this subscription subscript means that it is anion. We are talking about into delta t into A.

This is the volume in which we are looking into. So, the other side of the window will also contribute similarly. So, we can have the for current calculation eventually we want to measure the current because we have when there is a charge which is moving like ions then you want to find the current. So, in the calculation of current, all the cations within the distance of s delta t whose volume is s delta t into A will be passing through that area of interest A ok.

Similarly, if I have to talk about anions, anions will be moving from this side or inside to this one and that will be having a volume element of; even in this volume how much a number of currents ions are there needs to be understood. So, instead of plus sign we will just have a negative sign. How to derive the current we take up in the next class.

Thank you so much.