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

Lecture – 22
Molecular Motion in Liquids (Contd.)

Welcome to the 22nd lecture of Molecules in Motion. If you remember what we discussed in the last class was essentially on ionic mobilities, we are discussing sections on Molecular Motions in Liquid.

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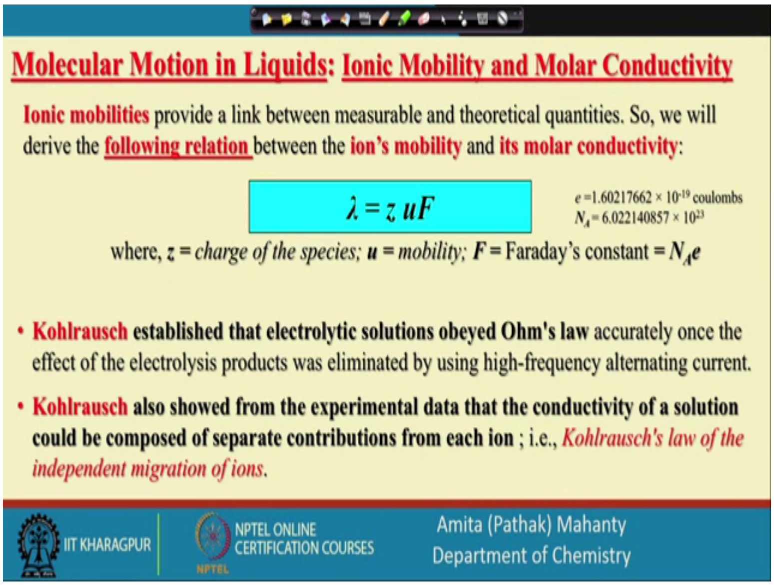

Molecular Motion in Liquids: Ionic Mobility and Molar Conductivity

Ionic mobilities provide a link between measurable and theoretical quantities. So, we will derive the **following relation** between the **ion's mobility** and **its molar conductivity**:

$$\boxed{\lambda = z\,uF}$$

$e = 1.60217662 \times 10^{-19}$ coulombs
$N_A = 6.022140857 \times 10^{23}$

where, z = *charge of the species*; u = *mobility*; F = Faraday's constant = $N_A e$

- **Kohlrausch established that electrolytic solutions obeyed Ohm's law** accurately once the effect of the electrolysis products was eliminated by using high-frequency alternating current.
- **Kohlrausch also showed from the experimental data that the conductivity of a solution could be composed of separate contributions from each ion** ; i.e., *Kohlrausch's law of the independent migration of ions.*

So, what we had talked about in the last class was regarding the ionic mobilities of the various ions. We talked about the bulky ions, we talked about the small ions and we had talked about in the last very last class we had talked about how the conductivity takes place due to and the associated mobilities with the small ions such as the hydrogen ion and the hydroxyl ion.

We had discussed how their conductivities or mobilities are different from the rest of the ions which we had discussed previously because of their way of mobility or movement of the ions through the solvent medium. They are essentially do not really roll over through the medium which we are looking into but they operate or move through the hop jump mechanism. Particularly we talked about the H plus ion, the proton in which you have if you have a hydrogen bond system.

Then how the H plus ion proton is transferred to the neighboring adjusting ion hydrogen molecule and how the hydrogen molecule is unfavorably oriented. And they orient in favor to have a 90 degree rotation; so that you have a transfer of the proton ion possible through the chain of the water molecules.

And this is one of the mechanisms which has been not very fully understood, but we have accepted that the Grotthuss mechanism which we discuss was the basis of the movement of ions such as H plus and OH minus and H plus in ammonium system H plus and OH minus in aqueous medium. So, we have talked in detail about the ionic mobilities and we are going to see how the ionic mobilities can provide a link between something which we know, which we have derived theoretically and something which is measurable, because until you have something measurable you really cannot talk about the properties and cannot verify them.

So, what we are going to be doing? We have already discussed this expression previously and the how the ionic mobility is going to be related to the molar conductivity. This is the molar conductivity which we are looking into, the lambda. How is that going to be related to the ionic mobility through this expression, where z is the charge of the species and F is the Avogadro constant, which is going to be nothing but the Avogadro number multiplied by the charge of the electron ok.

So, what we are going to look in today's lecture which we had initiated in the last lecture is how we are going to derive this expression, because this is going to give us some measure of the movement of the ions, and how we can interpret the results in terms of the measurable parameters in terms of whatever theories we have developed so far. So, in the process what we are going to be doing is we are going to look into the two points which we have pointed out here. We have will derived this expression for electrolyte system and as Kohlrausch's established that a electrolyte system will obey the Ohm's law. What is the Ohm's law? It is equal to V equal to I by R.

So, this is what we are going to see how whether whatever we have derived, whatever we expressions we have for that electrolytic solution whether Ohm's law is going to be applicable? Since, it is shown by Kohlrausch's that the Ohm's law will be valid only if the effects of the electrolysis product. If you are having a electrolysis system, so, if the electrolysis products are eliminated by using a high frequency alternating current only then we can verify the Ohm's law.

And we are going to be using that and showing that it how it can be assuming that we are using high frequency alternating current as the measuring parameter. If we use that how we can establish that the Ohm's law is well valid and second what all Kohlrausch's law Kohlrausch's also showed through experimental data, the conductivity of the solution is composed of this separate contribution from each of the ions; which we have already discussed Kohlrausch's law of an independent migration of ions. This is what we are going to eventually verify when we are done with the derivation of the lambda equal to z u F. So, let us begin with the derivation for this one.

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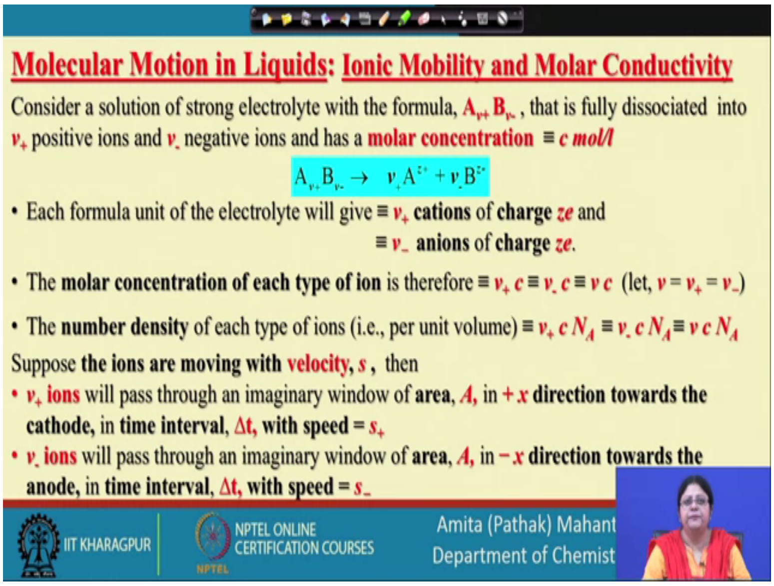

Molecular Motion in Liquids: Ionic Mobility and Molar Conductivity

Consider a solution of strong electrolyte with the formula, $A_{\nu+}B_{\nu-}$, that is fully dissociated into ν_+ positive ions and ν_- negative ions and has a **molar concentration** $\equiv c\ mol/l$

$$A_{\nu+}B_{\nu-} \rightarrow \nu_+A^{z+} + \nu_-B^{z-}$$

- Each formula unit of the electrolyte will give $\equiv \nu_+$ **cations** of **charge** ze and $\equiv \nu_-$ **anions** of **charge** ze.
- The **molar concentration of each type of ion** is therefore $\equiv \nu_+ c \equiv \nu_- c \equiv \nu c$ (let, $\nu = \nu_+ = \nu_-$)
- The **number density** of each type of ions (i.e., per unit volume) $\equiv \nu_+ c N_A \equiv \nu_- c N_A \equiv \nu c N_A$

Suppose **the ions are moving with velocity**, s, then

- ν_+ **ions** will pass through an imaginary window of **area**, A, in $+x$ **direction towards the cathode,** in **time interval,** Δt, **with speed** $= s_+$
- ν_- **ions** will pass through an imaginary window of **area**, A, in $-x$ **direction towards the anode,** in **time interval,** Δt, **with speed** $= s_-$

What we are going to do? We are going to start with the electrolyte system. Suppose let us consider a strong electrolyte, strong electrolyte means they will be completely dissociated in the solvent medium we are looking into. Suppose the electrolyte has a formula something like this A v plus into B v minus ok. It is a simple system A and B, if system where you have the nu plus 1 and nu minus 1 as the cation and the anion formula units, ok.

So, they are fully dissociated and if they are fully dissociated then according to the dissociation you see the nu plus is the number of cations which is going to be generated and nu minus is going to be the number of anions that is going to be generated. So, they are dissociating such that nu n nu plus positive charges are generated and nu minus negative charges are generated and let us consider that the electrolyte has a concentration molar concentration of c; that means, c moles per liter ok. So, each of the formula units of the electrolyte will give me how much? It will give me the charge of the ion which is associated its ze. So, if I am looking into the formula unit of the electrolyte then I should get nu plus number of cations of ze plus charge and nu n nu minus number of anions of charge ze right.

Since, we have the molar concentration of the electrolyte to be c. So, the molar concentration of each type of ions will be what? The number of ions of the formula unit which you have, this is the formula unit which you have, number of ions is here; cation is nu plus and anion is nu minus.

So, the total number of cation and total number of anion will be this into the concentration of the solute right because the concentration of the solute is c. So, the number of ions which is going to be generated positive ions will be; since if each formula unit is giving you a nu plus. So, the total charges of positive charges in the system will be nu plus into the concentration.

And similarly, you will have nu minus into the constant as a total number of anions which is going to be present. And since the system has to be electric electrically neutral then what happens? The total number of positive charge in the system nu plus into c should be equal to nu minus into c. For avoiding the plus and minus sign as subscript, let us represent the charge ion as nu. To avoid the complications of a subscript of minus and plus, we are avoiding the subscript and putting a positive nu here; where, I have put assumed that nu equal to nu plus equal to nu minus ok. Wherever we have when whenever we eventually want to put in the values, according to which type of ions we are looking into we can substitute nu by nu plus and nu minus without changing with that will not change the total final expression ok.

So, when what we have found out? The total number of molar concentration of the each ions, in the system is known now. And what will be the number density of each ions? A number density is the number of ions per unit volume or meter cube. So, this is moles per liter; this is in moles per liter ok, then number of moles which we are looking into if you want to find out what is going to be the total number of molecules or total number of ions then that many into the c concentration can be replaced by the Avogadro number ok.So, if I multiply with the Avogadro number, I get the total concentration in terms of the number. So, that is known as the number density of the ions in per unit volume of the solution which we are looking into.

So, since here also you see the total concentration total number density will be nu plus into c into the Avogadro number, this will be the same as a number of anions which will be a negatively charge ions which will be form. So, again I am assuming to avoid complications of the subscript of plus minus I am avoiding that to take it as a simple nu c N A ok. We must remember whenever we are taking nu, we are actually either taking N A plus or N A nu plus or nu minus according to the requirement of the charge we are looking into.

But for simplification, we will represent that by nu c N A; this is the total number of molecules or number density of the molecules present in the of the ions in the solution system of a unit volume ok, meter cube unit we can look into ok. So, per unit volume what whatever the number of ions are going to be present that we represent as the number density. Here this is they were supposed to be with moles, I am the multiplied by the Avogadro number.

So, whatever I have now, it is now in it was in liter. So, here also we are looking into a meter cubes sort of a volume. So, in unit volume what will be the number of ions present that is? That is what we call as the number density. We have done this discussed this previously also. Now, we are going to be looking into the ions which are moving with the velocity s.

In the last class, we have derived the expression of the ions moving under the electric field when they are moving with the electric field balanced with that of the viscous drag, we said they approach the final terminal velocity which we know also known as Stokes law. According to Stokes law, the final velocity or terminal velocity is also known as the drift speed.

So, we can say that the speed of the molecules ions which are moving under the electric field if that be represented as s then H nu plus ions will pass through an imaginary window of area A, say in the positive direction towards the cathode in delta time with the speed of s plus.

So, s whenever we are talking about s plus we have to understand that let us look is look at this diagram.

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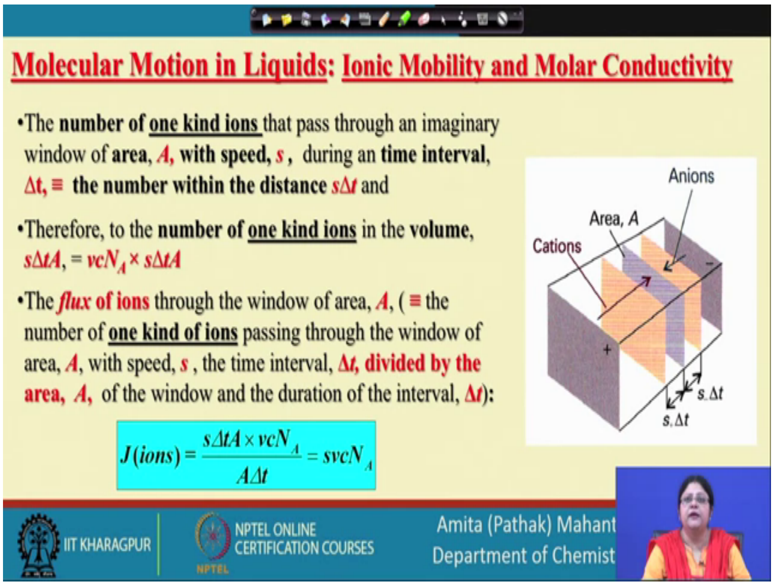

Molecular Motion in Liquids: Ionic Mobility and Molar Conductivity

- The **number of one kind ions** that pass through an imaginary window of **area, A, with speed, s**, during an **time interval**, Δt, ≡ **the number within the distance** $s\Delta t$ and
- Therefore, to the **number of one kind ions** in the **volume**, $s\Delta tA$, $= \nu c N_A \times s\Delta tA$
- The *flux* **of ions** through the window of area, A, (≡ the number of **one kind of ions** passing through the window of area, A, with speed, s, the time interval, Δt, **divided by the area, A,** of the window and the duration of the interval, Δt):

$$J(ions) = \frac{s\Delta tA \times \nu c N_A}{A\Delta t} = s\nu c N_A$$

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This is s plus, this is s minus of the movement of the ions. What we are looking into is how the anions and cations are moving towards the respective cathode or anode. So, when we are having; when we are saying that the speed of the ions is s plus what do we mean by that? That means, we are talking essentially of the cations, the number of cations which are present per formula unit is nu plus. So, nu plus ions are passing through a imaginary window of A and moving in the x plus direction towards the cathode plus charges move towards the cathode. That means, the they are moving towards the negative electrode in time interval delta t.

Similarly, if I have a subscript of s minus for the speed, the minus sign only represents that the negative charges negative ions that is the nu i types of ions will pass through a window of area A, in the negative opposite to the whatever x direction was towards the anode in delta time t ok.

So, the nomenclature is I suppose it is clear the sign H s plus and s minus is associated with the speed. So, then they do not have any sign as such. It is only to make us understand that whenever we are talking about s plus then we are talking about the speed of the ions which are positively charged and these positively charges are moving towards, if I say x positive towards the cathode the negative electrode. And when I say s minus; that means, the speed associated with the n negative charges or negative ions moving opposite to that direction of the positive charges towards the anode and in delta time t ok.

So, have a look at this. What is what is this thing which we are having? This is the positive electrode, this is the negative electrode. So, negative electrode is the cathode. So, what we are looking? We are looking as the positive charges are moving towards this side and negative charges are moving towards this side, ok.

So, what we are looking into? We are looking into a window with area A. This is a window which we are looking into. And now we are seeing the since electrons the charges are moving from this side to this side and this side to this side. So, if I am saying that the positive charges are into take consideration, then we are looking into a observing the movement of the charge through a window of area A and we are monitoring in delta time t.

So, the number of one kind of ions, it can be positive or negative I am not going to separate them in terms in terms of the subscript of plus minus to make it this expression simplified. So, the number of one kind of ions, it can be positive, it can be negative that passes through a imaginary window A; this is the A, during a time interval delta t is the total number of the number within the distance s delta t ok; s delta t s is the speed, delta t is the time.

So, if you understand that distance between a distance is s delta t because that that is from the Newton's law of motion; speed equal to distance by time. So, the distance is equal to speed into time. So, the whatever number of ions of any kind either plus or minus moving with the speed s, we are monitoring in the window A, whichever in the number of ions which is passing through the imaginary window with the speed s in delta time t will be the total number of ions which will be existing within this distance, this is the distance which we are looking into.

So, either this distance or this is for the positive charge and this is for the negative charge ok. So, when the negative charges are moving they are moving from this side and positive charges they are moving from this side to this side. We are not interested in the number of a types of charges right now. Let us take any one type of charge which is moving and if any one type of charges moving either with this distance within this distance will be number of ions within this distance, this is s delta t, if it is positive charges then s plus delta t and if it is negative charges then it is s minus delta t.

So, since we have tried to avoid the subscripts of sign plus minus, so, we have kept that as s and eventually if in the final expression if required we will change the signs of the associated with each of the charge. Say therefore, what next we can come to the number of kinds of number of the same type of ions which is which we have looked into in the first step. The number of ions passing through the imaginary window A with the speed s, in time interval delta t, the same one the number of ions in this volume element, this is the volume element, we initially we talked about the distance this distance.

Now, in this volume element, how many ions are going to be there which is going to be how many this is the area which we have, this is the distance into area, this is the volume you have. And what is the total number of ions associated? The number density we have already calculated. So, the number density into the volume element which we have is going to give you the number of molecules of one kind in this volume s delta t into A, ok.

Now, from here we want to find of the flux of ion which is passing through the window A. And how is the flux defined? The flux of any one kind of ion passing through the window of area A with a safe speed s in time interval delta t divided by the area A of the window divided by the duration of time ok. That is how the flux is defined we divided by the area divided by the duration of time.

So, what we have? We have one kind of ions either positive or negative passing through the window is through the contained in the volume element. All of them will be passing through the window A. So, what is the total number of particles associated? It is the total number density then nu into c into Avogadro number into the volume element s delta t into A. So, this divided by the area divided by the time interval will give you the total flux of ions.

So, this is what we have got. The flux of ion is nothing but the ratio this value, number density into the total volume element divided by area into delta t. What happens? We have the area and delta t cancelled off. So, what we get is that number of ions the flux of ions passing through a window A in delta time t of a particular kind of ion is nothing but the drift speed into the a number of ions per formula unit nu into the concentration molar concentration of the electrolyte into the Avogadro number.

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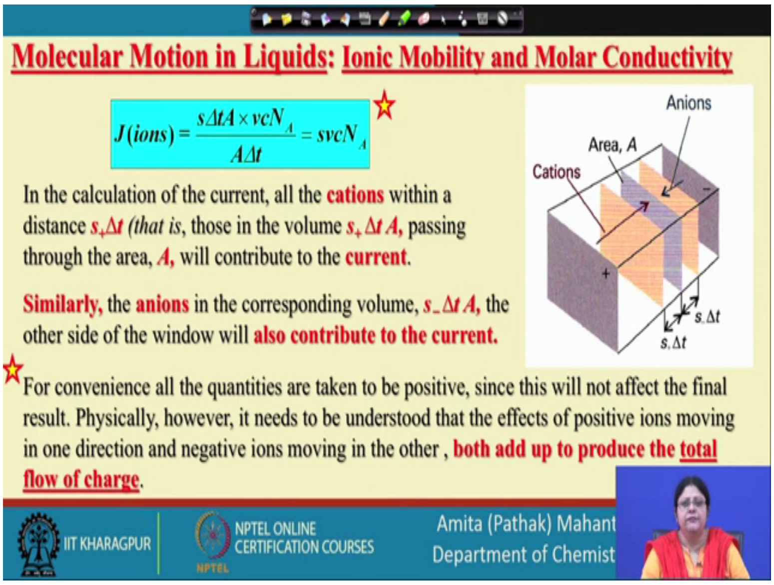

Molecular Motion in Liquids: Ionic Mobility and Molar Conductivity

$$J(ions) = \frac{s\Delta tA \times vcN_A}{A\Delta t} = svcN_A$$

In the calculation of the current, all the **cations** within a distance $s_+\Delta t$ (*that is*, those in the volume $s_+\Delta t A$, passing through the area, A, will contribute to the **current**.

Similarly, the **anions** in the corresponding volume, $s_-\Delta t A$, the other side of the window will **also contribute to the current.**

For convenience all the quantities are taken to be positive, since this will not affect the final result. Physically, however, it needs to be understood that the effects of positive ions moving in one direction and negative ions moving in the other , **both add up to produce the total flow of charge**.

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Department of Chemist

So, this is what we have in the calculation of the current. Now we want to find out the total current. So, the in the calculation of the current all the cations within the distance within this distance delta s plus into delta s plus into delta t that is those contain in this area in volume element into A, passing through a area A will contribute to the current.

That means, what I am trying to say all of the ions contained in this volume element and if it is a positive cations. Then, that means the distance which we are looking in will be s minus s plus delta t into A will be the total volume element, will contribute to us the ion because of the movement of the ions, they will contribute to the current.

Similarly, the anions corresponding to the volume element this one; this is the volume element content in this in between this window that is distance is s delta t into the total area of the window A. All the ions contained in this will which is trying to move this side will also contribute to the current. So, for convenience we have taken only the positive charge nu, but for all quantities which we have taken is actually if you understand physically. If you want to understand physically then you have to understand that effects of positive charge moving to in one direction and the negative charge moving in the opposite direction both need to be added up summed up to get the total current or total flow of charge ok.

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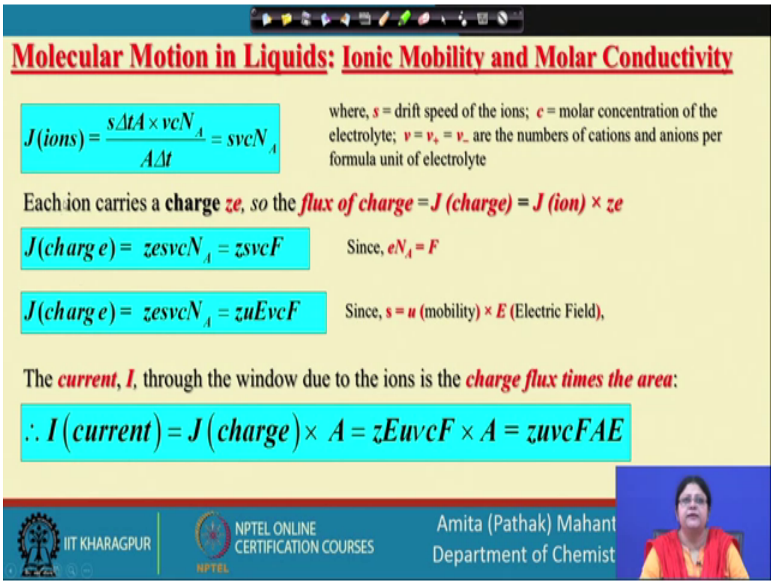

Molecular Motion in Liquids: Ionic Mobility and Molar Conductivity

$$J(ions) = \frac{s\Delta tA \times vcN_A}{A\Delta t} = svcN_A$$

where, s = drift speed of the ions; c = molar concentration of the electrolyte; $v = v_+ = v_-$ are the numbers of cations and anions per formula unit of electrolyte

Each ion carries a **charge** *ze, so* the *flux of charge* = *J (charge)* = *J (ion)* × *ze*

$$J(charge) = zesvcN_A = zsvcF$$

Since, $eN_A = F$

$$J(charge) = zesvcN_A = zuEvcF$$

Since, $s = u$ (mobility) × E (Electric Field),

The *current*, *I*, through the window due to the ions is the *charge flux times the area*:

$$\therefore I(current) = J(charge) \times A = zEuvcF \times A = zuvcFAE$$

So, if I have this, this is the expression which we have just now obtained for the flux of ion; where s is the drift speed, A is the area of window, delta t is the time. So, if the delta t and time is cancels; So what we have left with is the expression of drift speed into the nu is the can be positive a nu it can be negative nu we have taken as the nu for understanding are avoiding the complications of sign in the subscript. These are representing the total number of cations and anions per formula unit of the electrolyte into the Avogadro number.

So, now we want to find out what is the charge associated with it because ultimately we want to find out the current which is a measurable thing. So, we want to find out the current. So, before that we need to know what is the charge. The flux of charge is the charge will be nothing but the flux of ion into the charge ze.

So, if you have this unit the flux of ions which is derived, now you multiply this with the charge ze will you will give you the flux of charge. So, flux of charge is nothing but the flux of ion multiplied by ze, this is the expression you get. Here, you replace the N A into the e multiplication of N A into e as F, which is the Avogadro constant.

And the charge with flux of charge can be represented again if you replace s, s is the drift speed. And if you remember drift speed is nothing but the mobility into the electric field. So, mobility is u and electric field applied across is e. So, I can replace u in this expression with the mobility. If I replace u with the mobility, then I have a term which is relatable to the number of ions and that can be that multiplied by this electrics field will give you the expression for total charge and total flux of charge.

So, if we if you just look at this expression, this is the total flux of charge which we have this is the flux of charge z into u into the electric field applied, nu is the number of cations or anions per formula unit of the electrolyte, c is the concentration of the electrolyte and F is the Avogadro Faraday constant.

So, now if I want to if I know the flux of charge then I can find out the current. What is the current? Flux of charge times the area A will be giving you through the current is passing through a window of unit area A. So, if I multiply the flux of the charge into the area of that window, then I will get the current.

So, the current will be defined nothing but the charge flux into area. If you substitute here and you will get the z u v into c into F, Avogadro constant into the area of the window into A, ok; so this is the expression which we are getting for the current.

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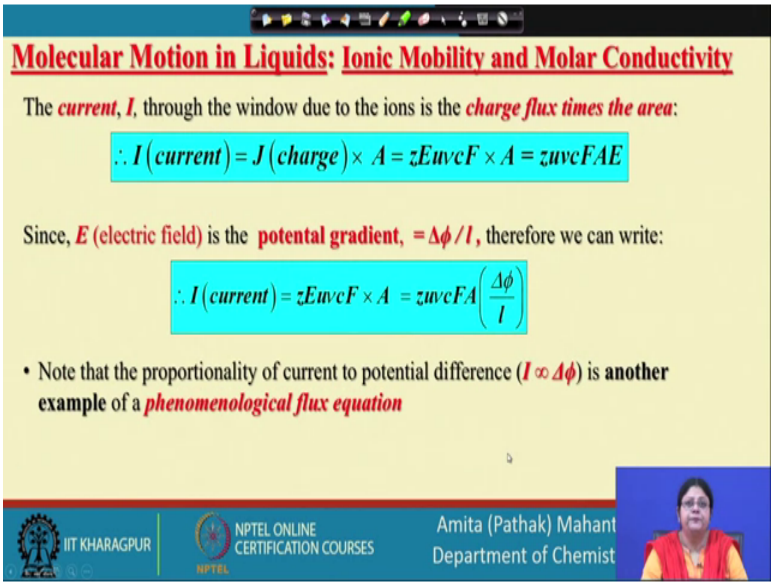

Molecular Motion in Liquids: Ionic Mobility and Molar Conductivity

The *current*, *I*, through the window due to the ions is the *charge flux times the area*:

$$\therefore I\left(current\right) = J\left(charge\right) \times A = zEuvcF \times A = zuvcFAE$$

Since, *E* (electric field) is the **potental gradient,** $= \Delta\phi / l$**,** therefore we can write:

$$\therefore I\left(current\right) = zEuvcF \times A = zuvcFA\left(\frac{\Delta\phi}{l}\right)$$

- Note that the proportionality of current to potential difference ($I \propto \Delta\phi$) is **another example** of a *phenomenological flux equation*

The current through the window of the ions is thus this expression. Now, if you look at the e value, the electrical field which is applied it is nothing but the potential gradient which is nothing but d phi by l, the potential between two ends and l is the distance between the two ends of the electrode. So, this can be the e electric field can be associated or related to the potential gradient.

So, if I can replace the potential gradient e with the potential gradient d phi by l, then the expression which I get is current I equal to z u v into c into F into A into the gradient of potential. So, see I have related I in terms of the electric field, now I am relating the I with respect to the potential gradient. And, if you look at this expression, here you have something which is some similar to what we have discussed in previous classes. And here we have the flux equation related to the current in terms of being proportional to the potential difference.

So, potential difference is what is driving the current to flow and this is how we are going to be if you recapitulate the equations which we had derived for the phenomenological flux equation. Here we have I proportional to the delta phi delta phi is nothing but the potential gradient which we have potential difference which we have and the two electrode points. So, the charge which is going to flow or the current which is going to flow is going to be proportional to the potential difference at the two ends of the electrode that will be the driving force.

So, in the next class we will look into how these parameters can be how each of the ions and how much each of the ions are going to carry a current is going to be carried by each ion. And then also we are going to relate the mobilities of these. And we will verify the Ohm’s law and whatever the Kohlrausch’s law which we had derived. We had said that can be applicable to a system which is charged and moving under a electric field.

Thank you so much.