# Molecules In Motion
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## Lecture – 29
## Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules In Motion.

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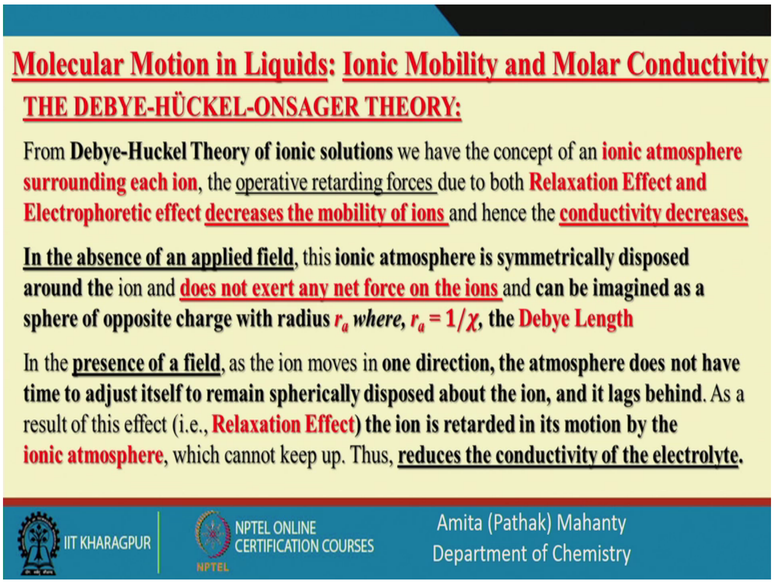

**Molecular Motion in Liquids: Ionic Mobility and Molar Conductivity**

**THE DEBYE-HÜCKEL-ONSAGER THEORY:**

From **Debye-Huckel Theory of ionic solutions** we have the concept of an **ionic atmosphere surrounding each ion**, the operative retarding forces due to both **Relaxation Effect and Electrophoretic effect** **decreases the mobility of ions** and hence the **conductivity decreases.**

**In the absence of an applied field**, this **ionic atmosphere is symmetrically disposed around the** ion and **does not exert any net force on the ions** and **can be imagined as a sphere of opposite charge with radius** $r_a$ *where*, $r_a = 1/\chi$, **the Debye Length**

In the **presence of a field**, as the ion moves in **one direction, the atmosphere does not have time to adjust itself to remain spherically disposed about the ion, and it lags behind.** As a result of this effect (i.e., **Relaxation Effect**) **the ion is retarded in its motion by the ionic atmosphere**, which cannot keep up. Thus, **reduces the conductivity of the electrolyte.**

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So, in the last class we were discussing about the Debye Huckel Onsager theory and what we had talked about was the 2 type of forces that are operative on the charged particle; particles like ions in electric field.

Actually retard the motion of the molecules or motion of the ions and the 2 types of effects which we had talked about was the relaxation effect an electrophoretic effect; which was eventually responsible for the ions to move slower. So, what we are actually looking into? We are trying to look into the Kohlrausch's law from where we had the molar conductance and dependence on the concentration in terms of under root c, where c is the molar concentration.

So, what we are trying to do like we had discussed the Debye Huckel theory as such in the last class of the system which is ionic solution. We had seen that the concept of

Debye Huckel theory is actually based on the concept of ionic atmosphere; that means, the surrounding ions counter ions around a central either positive or negative ion.

So, this ionic atmosphere surrounding each of the ion is actually responsible for the retarding forces that give rise to the effect; which we have discussed is the electrophoretic effect and the relaxation effect. And this forces this concept of ionic atmosphere surrounding a ion actually gives rise to the concept of decrease in mobility. And decrease in mobility is going to be in effect be what you say as a consequence to have a lower conductivity; molar conductivity.

So, when we are talking about the ionic atmosphere; we are talking about there the effects which we have seen.

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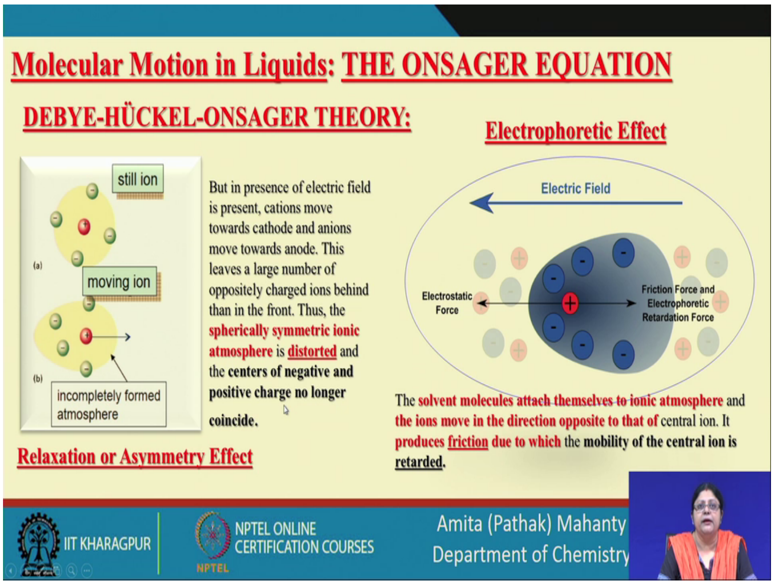

**Molecular Motion in Liquids: THE ONSAGER EQUATION**

**DEBYE-HÜCKEL-ONSAGER THEORY:**

But in presence of electric field is present, cations move towards cathode and anions move towards anode. This leaves a large number of oppositely charged ions behind than in the front. Thus, the **spherically symmetric ionic atmosphere** is **distorted** and the **centers of negative and positive charge no longer coincide.**

**Relaxation or Asymmetry Effect**

**Electrophoretic Effect**

The **solvent molecules attach themselves to ionic atmosphere** and **the ions move in the direction opposite to that of** central ion. It **produces friction due to which** the **mobility of the central ion is retarded.**

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If you just can go back and see the type of effects which we have in when we are talking about the ionic effect; we had talked about the isometric effect that is a relaxation effect and the electrophoretic effect. What was the condition which we had visualized when we had a asymmetric effect or a relaxation effect?

We are the basis of the whole discussion was that a central ion is surrounded by count outnumbered number of counter ions of opposite charges surrounding it and this forming the ionic atmosphere. So, in this is a condition when you do not have a electric field; we have a ionic atmosphere which is perfectly symmetric. The center of the positive ion and the center of all the counter ions will coincide.

So, you will have a perfect symmetric looking spherical atmosphere; if there is a no electric field applied, but when what happens when you have an electric field applied? What is in most of the positive ion or the negative ion, whichever the central ion is will be moved moving towards the electrode. Like positive ion is going to move towards the negative electrode like cathode and in the movement what happens?

They disturb the symmetric ionic atmosphere surrounding it because what happens when it is moving forward the charge is the central charge is moving forward it does not have enough sufficient time to form the new ionic atmosphere.

But what happens that the one which were from which it is trying to come out is going to be distorted and the center of the positive ion will no longer coincide with the whatever negative charges are there. Or if it is a counter ion whatever I the center of the counter ions will not match.

So, it is center of counter ions I am saying because if it is a positive charge then the surrounding ions are negative if it is a negative charge surrounding ions are positive. So, based on this we had said that asymmetry is formed in the ionic atmosphere and we call this is as a ionic a asymmetric effect or relaxation effect.

So, what is happening? The negative charges of the counter ions which has which was initially there in the ionic atmosphere will try to pull it; pull the central movement of the central ion towards the cathode. And this in this process the movement of the central ion is going to get reduced. Similarly, we had talked about the electrophoretic effect; electrophoretic effect what we know because of the presence of ions and these ions are surrounding the central ion.

Suppose we are having positive ions surrounded by a negative ion; usually this will be a symmetric one. And what happens when they are in a solvent these ions will interact with the solvent molecules which are present. So, what happens the not only the ion, but also the; what do you say the ionic atmosphere will tend to interact with this surrounding solvent molecules.

So, the solvent molecules get attached to the ionic atmosphere and the ions and when what happens when you are having applied electric field; suppose the positive charge is moving towards the cathode under the electrostatic force, what happens? The ionic atmosphere which is not completely disappeared from the previous one; previous position will tend to pull the ion back. But also in the process we will have the solvent molecules attached to it and this solvent molecules give rise to will give rise to a viscous drag.

So, this viscous drag which is going to be operative on this ion which is supposed to be moving under the electric field towards the respective electrode will be now reduced. So, this; these are the 2 effects which we have talked about in the last class which is going to actually hamper the movement or the motion of the ions in a electric field. So, these are the 2 things which we had talked about which is going to be there when the ions are moving. So, these are the retarding forces which are acting on the ion when they are moving.

So; how do we establish? This was what we have understood we have put forward; now we need to formulate. We need to formulate a new equation which is going to match whatever concept which we have we are talking about with that of what is the observed.

So, we are going to look into a the generating a new equation which will be the modification of the Debye Huckel theory and that will be called as the Debye Huckel Onsager theory and the equation corresponding to that will be called as Debye Huckel Onsager equation. So, what we are trying to do? We are trying to model a new equation; further modifying, cracking into account not only the ionic atmosphere which is operative around the central ion which is placed in a solution it is a electrolyte solution.

So, the central ion is of the salt which we are looking considering in this solution. And the forces which are operative on that ion is not only the ionic atmosphere; it is because of the ionic atmosphere, but it is the effects which are generated because of the ionic atmosphere the relaxation effect and the electrophoretic effect.

Now, what are the things which is going to increase or decrease the electrophoretic effect which we see in a particular ion ok. So, we have a ion central ion surrounded by counter ions. So, what happens when we have a electric field and what we happens when we do not have a electric field and how each of them is going to effect the relaxation effect and the electrophoretic effect what are the parameters which are going to effect the relaxation effect and electrophoretic effect in a particular system is what will be the basis of deriving an equation which should be applicable to any type of electrolyte which we are looking into.

And should be matching whatever we do through experiment and get the results. So, whatever experimental results observations which we have we are going to try to now modify the equation of the Debye Huckel and make it the modification will be known as the Debye Huckel Onsager theory. And this new equation we will test or validate is how much of this equation is going to be in sync with that of what is observed in experimental when we do the experiment.

So, let us come down for each of the effects which will be contributing. So, in absence of an electric field; so, in absence of a electric field what we have? The ion still will be having ionic atmosphere and this ionic atmosphere will be symmetrically disposed around the ion. So, there will be no net force on the ion because it is symmetrically disposed and although the magnitude of all the surrounding counter ion should be should be equal to the force which is operative on the negative charges should be balancing the positive charges in the solution.

So, you have a electro neutrality in the solution. So, we can imagine a sphere suppose we imagine a sphere which is ionic atmosphere for a any particular ion. And suppose the radius if it is not under applied in electric field; we have a symmetric disposition of the ionic atmosphere let that radius be r a; let us that call that radius of the ionic atmosphere with surrounding the central ion be r a; which is can be given as 1 by chi where the this as the Debye length.

So, we have defined r a as a new parameter which we have introduced we have introduced the r a as the ionic atmosphere; when the ions are the counter ions are symmetrically disposed around the central ion and there is no net force on the ion as per say. So, and the electro neutrality is maintained so, the radius r of that sort of a ion will be taken to be 1 by chi, where chi is the Debye length.

Now, in presence of a field as the ion start moving in one direction, the atmosphere does not have time to adjust to itself to remain spherically disposed around the ion and it lags behind. As a result of this we have this is the effect we called as a electro relaxation effect or asymmetric effect. The ions which is gets which is in motion gets retarded by the ionic atmosphere.

So, this relaxation effect will actually reduce the movement of the ions under the electric field and this will result in the reduction in the conductivity of the electrolyte. So, this is what we have discussed; so, let us see what are the parameters which is going to effect this relaxation effect which is operative which is actually lowering the speed of the ions when under the electric field.

So, what we had talked about? The parameter r a is the radius of the ionic atmosphere, when the counter ions are symmetrically disposed around the central ion and that is equal to 1 by chi; where chi is the Debye length. So, what happens? The effect of ionic atmosphere; what will it cause is lowered ionic atmosphere is actually causing a retarding effect on the motion of the ions right.

So, the effect of ionic atmosphere is lowered when the 1 by chi is large ok; that means, r a which we have defined as 1 by chi is large. What do you mean by the r a being large; r a being large means the ionic atmosphere is far away. So, the radius is the distance of the central ion to the; what do you call say haze of the counter ions. So, this radius which is the limits of the haze of the haze around of the counter ion around the central ion this radius if it is high; if this is high what does it mean? The ionic atmosphere is far away the distance bit is high.

So, what happens when the ionic atmosphere is far away? Then the effects caused by the ionic atmosphere should reduce right. So, whenever we have r; the radius which we have defined being equal to 1 by chi that is the Debye length; if the Debye length is high or large; that means, the ionic atmosphere are far apart. So, the f x which the ionic atmosphere generates on the central ion will be lowered.

So, the electro the relaxation effect or asymmetry effect will be effected if the ionic radius is large. Now what happens regarding the dielectric constant? What is the dielectric constant if you have the high dielectric constant; material or solvent with high dielectric constant what is example of that? Water has a very high dielectric constant around 80.

So, if you have a highly dielectric constant solvent with a very high electric dielectric constant because the forces between ion what happens? The ionic atmosphere effects of the ionic atmosphere is again lowered. Why the dielectric force a constant if it is having; it is a when the value is large, then the forces that are between the ions is going to be reduced by the dielectric constant of the solvent.

Because if you have dielectric higher dielectric constant they themselves will be having a separation of charge so, if you are going to have a very high dielectric constant as a solvent; then the ionic atmosphere which is supposed to be symmetrically disposed around the central ion will be; the effects of such a atmosphere will be lowered because now the force between the ions is going to be effected by the high dielectric constant of the solvent.

So, higher the dielectric constant of the solvent you are using; the ionic atmosphere which is formed; which will effects generated because of the ionic atmosphere like electrophoretic and the relaxation effect should be reduced. What happens when you have thermal energy associated with it? With what happens k T means as the thermal energy which is associated with a molecule or a ion.

So, if you have a very high; if you have a very high value of k T; then what happens? Then the ionic atmosphere gets disturbed. So, when you increase in the temperature; that means, the thermal energy is increased by increasing the temperature, then the disposition of ionic atmosphere is not coherent. So, the ionic atmosphere effects within the ionic atmosphere generates will be lowered.

So, what we have seen? If we look into only the effects which is going to which is whatever the parameters which are going to effect the relaxation effect; which is non symmetric disposition of the ionic atmosphere. What are the effects which what are the parameters which effect this ionic atmosphere will be effecting the effects which are generated because of the either electrophoretic effect or the relaxation effect.

Now, when we are talking about the relaxation effect here we have seen that the radius of the ionic atmosphere which is given to be 1 by chi, they do by length Debye length that is if that is going to be large; that means, ionic atmosphere is far apart; that the effects generated by ionic atmosphere like in relaxation effect is lowered. So, higher the r a;

lower will be the effects generated by the relaxation effect because the ionic atmosphere effects are reduced.

Similarly, if you have a solvent with a high dielectric constant because of the high dielectric constant the ionic atmosphere disposed around the central ion again will be disturbed. And so the effects which is going to be generated like relaxation effect due to the ionic atmosphere will also reduce. So, we can reduce the relaxation the effects of ionic atmosphere; if you reduce the say if we increase the r a the radius of the ionic atmosphere.

If the ionic atmosphere are large if the Debye length is large and if the dielectric constant of the solvent is large as well as if the temperature of the system is high. So, if you have high temperature higher dielectric constant and higher chi the r value; the Debye length value then you have a reduced effect on the relaxation the parameters effecting the relaxation effect is reduced.

So, the asymmetry effect and the or the relaxation effect thus reduces the molar conductivity. So, whatever associated parameters which we have since it is going to effect the motion of the ions; it is hence going to effect the mobility. So, say molar conductivity of the electrolyte and how are these disposed?

Suppose we say it is only because of the relaxation effect; then we say that the how we formulate the relation as B being effect generated because of the relaxation effect. And this B when if related to the molar conductivity, it should be something like this; B should be in relation to the molar conductivity will be B is a constant into the limiting value of molar conductivity into root c; for a 1, 1 electrolyte.

So, for a 1, 1 electrolyte the formulation of Debye Huckel Onsager theory is due to relaxation effect; this is the constant which we are going to have. And what are these; what are the parameters on which this B is dependent on? You just have a look at it you have B equal to 8.2 into 10 to the power of 5 divided by the dielectric constant of the solvent into the temperature raised to the power 3 by 2. So, the B parameter is dependent on the dielectric constant of the solvent and the temperature associated on the system.

Now, you have another parameter which should be now understood how it is going to effect the molar conductivity and that is the electrophoretic effect.

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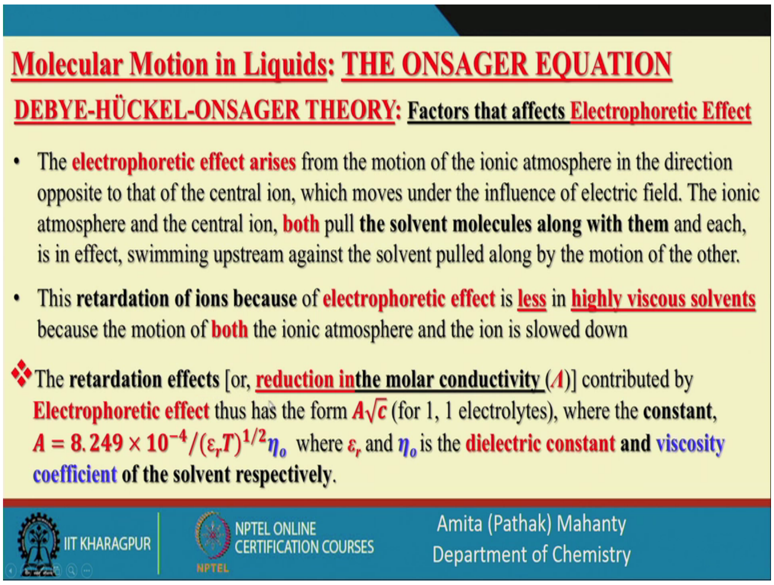

## Molecular Motion in Liquids: THE ONSAGER EQUATION

### DEBYE-HÜCKEL-ONSAGER THEORY: Factors that affects Electrophoretic Effect

- The **electrophoretic effect arises** from the motion of the ionic atmosphere in the direction opposite to that of the central ion, which moves under the influence of electric field. The ionic atmosphere and the central ion, **both** pull **the solvent molecules along with them** and each, is in effect, swimming upstream against the solvent pulled along by the motion of the other.
- This **retardation of ions because** of **electrophoretic effect** is less in highly viscous solvents because the motion of **both** the ionic atmosphere and the ion is slowed down

❖ The **retardation effects** [or, reduction in**the molar conductivity** ($\Lambda$)] contributed by **Electrophoretic effect** thus has the form $A\sqrt{c}$ (for 1, 1 electrolytes), where the **constant**, $A = 8.249 \times 10^{-4}/(\varepsilon_r T)^{1/2}\eta_o$ where $\varepsilon_r$ and $\eta_o$ is the **dielectric constant and viscosity coefficient of the solvent respectively**.

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So, the electrophoretic effect arises from the motion of the ions ionic atmosphere in the direction opposite to the central ion; which moves under the influence of electric field.

The ionic atmosphere and the central ion both pull the solvent molecules along with them; when they are moving. It is something like they are trying to move swim upstream against the solvent pull; by the this friction which is going to be pulling them back is because of the molecules being the solvent molecules being attached to the ions as well as the at ionic atmosphere.

So, that this causes a retardation in the movement of the ions because they are some it is like you are trying to somebody you are trying to swim upstream and somebody is trying to pull you back. So; obviously your speed of at which you can make through value of swimming is going to be effected if somebody is pulling you back.

The solvent molecules along with the ionic atmosphere which is not completely disappeared now; we under the application of electric field we tend to pull the molecules back. So, if they are trying to pull it back then the generated effect is going to be a retarding effect in the motion of the ions. And if there is a motion of the ions associated we will have a reduction in the molar conductivity.

So, the retardation of ions because of electrophoretic effect is less if the solution is of higher viscosity. The viscosity coefficient is high if the solvent which is medium which you are using has a high viscosity or high viscosity coefficient; then what you have? The retarding in effects of the ions because of the electrophoretic effect is reduced because motion of the ions is slowed down because of the highly viscous solvent ok.

So, the retarding effects which is which is reflected in the reduction in the molar conductivity due to electrophoretic effect can be say associated with the electrophoretic effect; can be represented by a term which is a formulations.

See these are all formulation, we are modeling it depending on what type of electrolyte we are using for a 1, 1 electrolyte it the Debye Hackel Onsager theorem proposed; that we if we have a constant A into root over c will be the contribution to the molar conductivity due to the retarding effects of the electrophoretic effect ok.

So, the electrophoretic effect associated with the ionic atmosphere when it contributes to the retardation or lowering of the molar conductivity can be given by this expression A equal to 8.249 into 10 to the power minus 4 divided by, you have the parameter which is dielectric constant temperature, but here it is raised to the power half into eta naught.

This is the new term which we have added when we are talking about the contribution of the electrophoretic effect towards the lowering of the molar conductivity. So, these are the 2 parameters which we have taken down.

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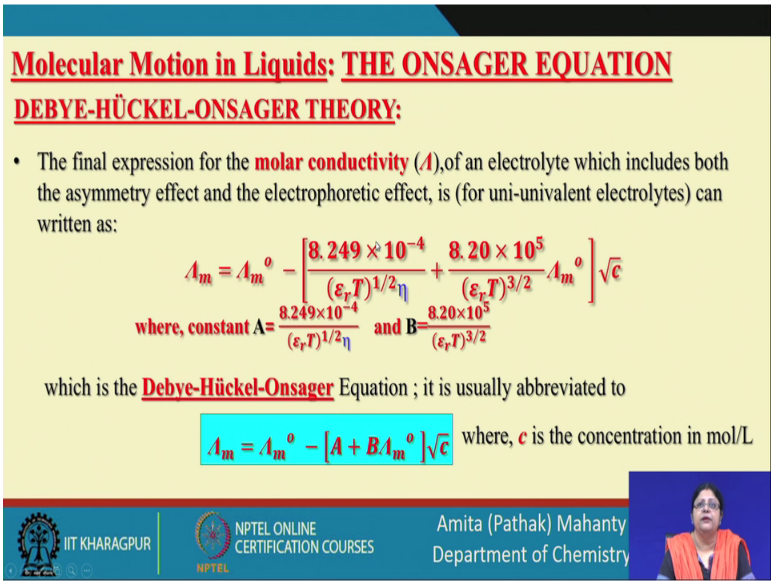

**Molecular Motion in Liquids: THE ONSAGER EQUATION**

**DEBYE-HÜCKEL-ONSAGER THEORY:**

- The final expression for the **molar conductivity** ($\Lambda$),of an electrolyte which includes both the asymmetry effect and the electrophoretic effect, is (for uni-univalent electrolytes) can written as:

$$\Lambda_m = \Lambda_m^{o} - \left[\frac{8.249\times10^{-4}}{(\varepsilon_r T)^{1/2}\eta} + \frac{8.20\times10^{5}}{(\varepsilon_r T)^{3/2}}\Lambda_m^{o}\right]\sqrt{c}$$

where, constant $A = \frac{8.249\times10^{-4}}{(\varepsilon_r T)^{1/2}\eta}$ and $B = \frac{8.20\times10^{5}}{(\varepsilon_r T)^{3/2}}$

which is the **Debye-Hückel-Onsager** Equation ; it is usually abbreviated to

$$\Lambda_m = \Lambda_m^{o} - \left[A + B\Lambda_m^{o}\right]\sqrt{c}$$ where, $c$ is the concentration in mol/L

So, if we want to write down the final expression which from the Debye Huckel Onsager theory; then we have the final expression will look something like this.

This both have the equation was if you remember if it is one was a root A under root c was because of the electrophoretic effect and another was the B lambda naught into under root c this was because of the relaxation effect.

So, if you take these 2 contributions then the final expression for molar conductivity which includes both the asymmetry effect and the electrophoretic effect for a 1, 1 electrolyte system; which is the simplest of system we can say that the molar conductivity at any concentration will be equal to molar conductivity at infinite dilution minus this is the term what is coming from the electrophoretic effect; the A term. A into under root c and the other one is the B term coming from the relaxation effect.

So, in that relaxation effect we had a lambda naught value. So, if you these are the 2 values which we have given as a constant; see these are constants which are generated after doing repeated experiments so that we can match with our experimental observations.

So, the final Debye Huckel equation which we can formulate after modification into taking into account the effects generated by the ionic atmosphere. And the like the electrophoretic effect and the relaxation effect, we get the equation something like this; lambda equal to lambda naught minus A plus B, where lambda naught into lambda naught and the whole raised to multiplied by under root c.

Isn’t this equation quite similar to what we had talked about in the Kohlrausch’s law? Kohlrausch’s law we had taken lambda for a molar conductivity at any concentration equal to molar conductivity at infinite dilution minus k under root c. So, the k which we had had in the previous; we have now tried to justify in terms of the electrophoretic effect. This is the electrophoretic effect and this is because of the relaxation effect associated with the ionic atmosphere of a electrolyte.

Thank you.