Molecules in Motion

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Lecture – 27
Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules in Motion.

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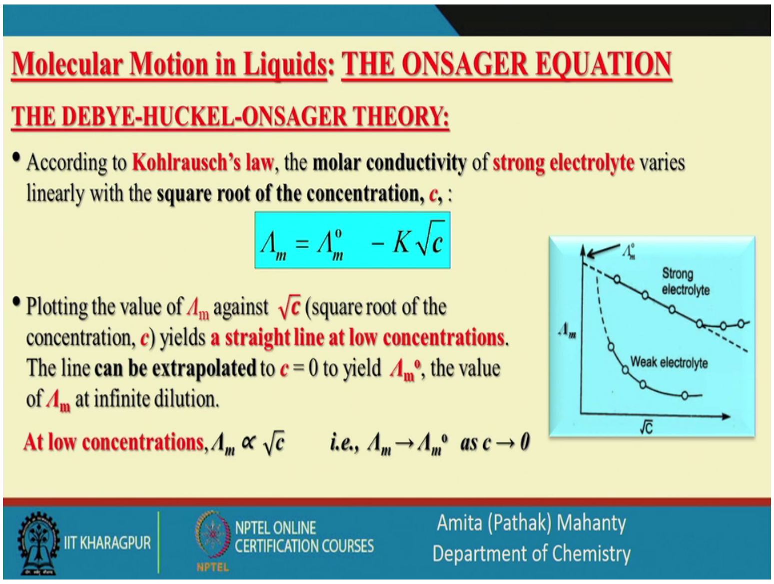

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HUCKEL-ONSAGER THEORY:

- According to **Kohlrausch's law**, the **molar conductivity** of **strong electrolyte** varies linearly with the **square root of the concentration, *c*,** :

$$\boxed{\Lambda_m = \Lambda_m^0 - K\sqrt{c}}$$

- Plotting the value of Λ_m against $\sqrt{c}$ (square root of the concentration, c) yields **a straight line at low concentrations**. The line **can be extrapolated** to $c = 0$ to yield Λ_m^0, the value of Λ_m at infinite dilution.

At low concentrations, $\Lambda_m \propto \sqrt{c}$ i.e., $\Lambda_m \to \Lambda_m^0$ as $c \to 0$

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And in this as we have discussed so far, in the last class also I was talking about this that we have talked about the conductivity molar conductivity of a strong electrolyte. What we are going to what we have seen according to the Kohlrausch's law. The molar conductivity of a strong electrolyte varies linearly with the square root of the concentration. If you remember this was the expression we had; that was the molar conductivity at any concentration was equal to the molar concentration conductivity at infinite dilution minus K under root of c. So, we have a square root of concentration dependence of the molar conductivity.

We had also seen that if you plot the molar conductivity under the square root of the concentration, this concentration is moles per liter. And if you get a straight line at very low concentrations and we can find out the value of the lambda naught. That is the molar conductivity at 0 almost tending to 0 concentration of the electrolyte. If we extrapolate this plot, then wherever it intersects the y axis at corresponding to 0 concentration we label that as the molar conductivity at infinite dilution.

So, what we have seen, that the molar conductivity is proportional to the square root of the molar concentration of the electrolyte. As the concentration of the electrolyte approaches 0, then the molar conductivity approaches, the molar conductivity at infinite dilution ok. This is what we have seen; this is some sort of a behavior which, we need to account for why is the molar conductivity of a strong electrolyte dependent not on this concentration, but under root of the concentrate concentration of the electrolyte.

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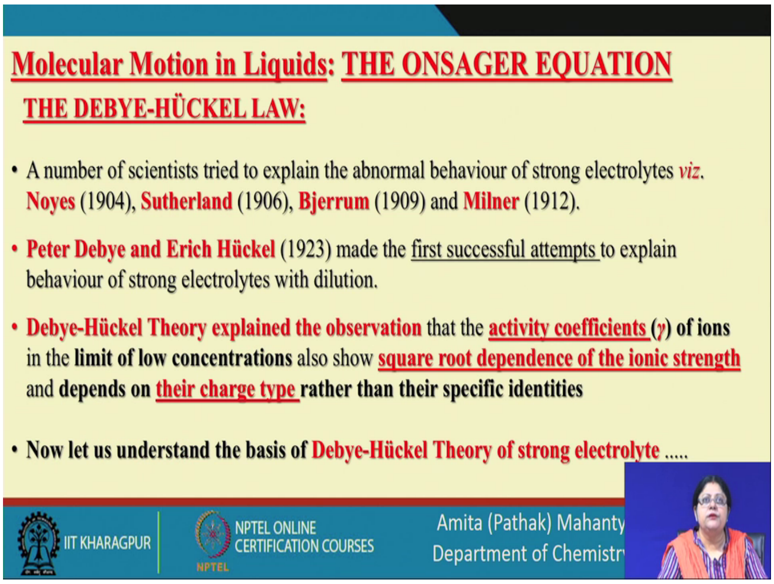

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL LAW:

- A number of scientists tried to explain the abnormal behaviour of strong electrolytes *viz*. **Noyes** (1904), **Sutherland** (1906), **Bjerrum** (1909) and **Milner** (1912).
- **Peter Debye and Erich Hückel** (1923) made the first successful attempts to explain behaviour of strong electrolytes with dilution.
- **Debye-Hückel Theory explained the observation** that the **activity coefficients** (γ) **of ions** in the **limit of low concentrations** also show **square root dependence of the ionic strength** and **depends on their charge type rather than their specific identities**
- **Now let us understand the basis of Debye-Hückel Theory of strong electrolyte** .....

So, if we go look into this a number of scientists have tried to explain the behavior of the strong electrolyte. And these are some of the scientists, Noyes and Sutherland, Bjerrum and Milner. These are if you see in the 1060's 19 with in 1912, in the first within 10 years of each other we have some sort of; explanation by the scientist. But the major breakthrough was when two scientist Peter what we have with do by Debye Erich Huckel. So, Peter Debye and Erich Huckel were the two scientist, who successfully attempted to be explain the behavior of a strong electrolyte when we have dilution.

What was the Debye Huckel theory? Whatever we have we are going to be looking into the Onsager equation, which is a further modification of the Debye Huckel theorem or the law which we have established. So, before you go into understanding what is the what are the things which we have added when we are talking about the Onsager equation. Before that let us talk about the Debye Huckel theorem, what was the observation? The Debye Huckel theorem the main observation which was explained was by Debye Huckel theorem is the activity coefficient of ions, when you have ions in solution; we are expressing the activity of the instead of concentration we have activity coefficient of the ions. Activity of the ions represented where you have the concentration equal to activity equal to concentration into the activity coefficient if you remember.

So, what we have what the explanation was given by Debye Huckel theorem or the theory is the activity coefficient of ion, which are ions in solution the electrolytes. In the limit of low concentration also showed a square root dependence on their ionic strength and they also found that the dependent on the type of charge that was involved not the specific identity of the charge. So, let us now understand what the Debye Huckel theory for a strong electrolyte was supposed to be.

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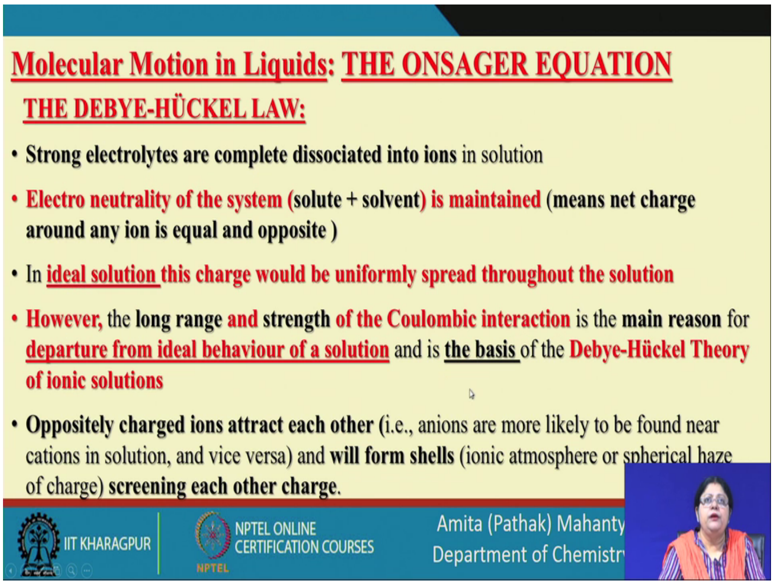

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL LAW:

- **Strong electrolytes are complete dissociated into ions** in solution
- **Electro neutrality of the system (solute + solvent) is maintained (means net charge around any ion is equal and opposite)**
- In **ideal solution this charge would be uniformly spread throughout the solution**
- **However,** the **long range and strength of the Coulombic interaction** is the **main reason** for **departure from ideal behaviour of a solution** and is **the basis** of the **Debye-Hückel Theory of ionic solutions**
- **Oppositely charged ions attract each other** (i.e., anions are more likely to be found near cations in solution, and vice versa) and **will form shells** (ionic atmosphere or spherical haze of charge) **screening each other charge**.

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So, for a strong electrolyte we all have discussed this before, for a strong electrolyte the ions are supposed to be completely dissociated in solution. And the solution itself the composed of the solute and the solvent is supposed to be having electro neutrality. They are going to no there is no going to be a net positive or negative charge, we have to we have the solution maintained at they are electrically neutral.

If we talk about ideal solution, ideal solution when you have a solute; the electrolyte in a solvent the ideal solution will be having the uniform spread of the charge throughout the solution. But what Debye Huckel proposed or interpreted as then he formulated the theory, is the long range and the strength of the columbic interaction is the main reason for the solution to deviate from their ideal behavior and this is the basis of the Debye Huckel theorem ok.

So, opposite charge ions attract each other we have the anion whenever we have a solute electrolyte dissolved in a solvent they will dissociate into positive and negative ions. So, opposite charge ions attract each other what happens the anion is more likely to be found near a cation in a solution and vice versa. And in the form they form a shell sort of a thing which is sort of a haze of opposite charges around a central charge. So, the this haze which is supposed to be a symmetric around a central charge actually screens the charge of the central ion.

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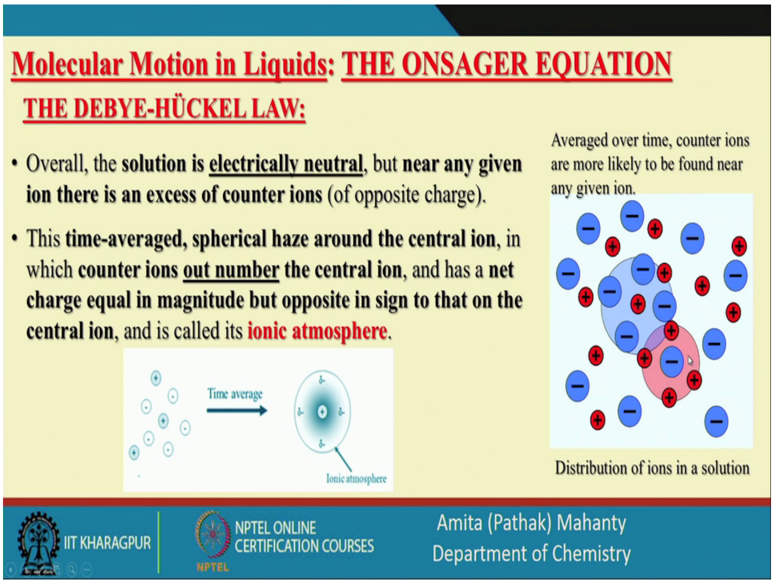

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL LAW:

- Overall, the **solution is electrically neutral**, but **near any given ion there is an excess of counter ions** (of opposite charge).
- This **time-averaged, spherical haze around the central ion**, in which **counter ions out number the central ion**, and has a **net charge equal in magnitude but opposite in sign to that on the central ion**, and is called its **ionic atmosphere**.

Averaged over time, counter ions are more likely to be found near any given ion.

Distribution of ions in a solution

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So, what we are looking into? We are looking into something like this, where this is the distribution of ions in solution and you see the positive charges are majorly surrounded by the negative charges. And this charge this is a central charge, this is the central charge, this is a negative charge, which is surrounded by a positive haze and a positive charge is surrounded by a negative haze. So, the overall solution is electrically neutral, but for by in any given ion you will have at any point any given ion, will excess have excess of counter ion, opposite ion, are surrounding them. And the if you take a time average of counter ions are more likely to be found near the given central ion.

If you take a time average the spherical sphere haze which we are looking into see I have I demarcated this as a blue haze. And this haze around the central ion of the counter of the counter ion here outnumbers and a central ion. And the net charge is equal to the magnitude, but in opposite to the central charge of the central ion. So, what we have you see the time average, these are the dispersions you have the ions which we have. If we take a time average take a time shot and we are likely to encounter a haze of oppositely charged ions against a central ion of opposite charge.

If you have a central ion of positive charge, that is going to be surrounded by negative charge; in a spherical manner ok. And this haze around the central ion this can be a negative ion as well then you will have the positive ion haze around it. Always we have seen that the number of counter ions are surrounding the central ion is going to be outnumbered.

The haze forming and the ions forming the haze around the central ion will always outnumber the ion in the center. That is what we are seeing in this dispersion as well and this one as well ok. Whether it is negative ion or positive ion they will be surrounded by haze of oppositely charged ion will which will have which will be more than the outnumber the number of the central ion. If central ion is one we see a surrounding at least four or five ions here. So, this haze this symmetric haze around the central ion taken on over a time average is known as the ionic atmosphere ok.

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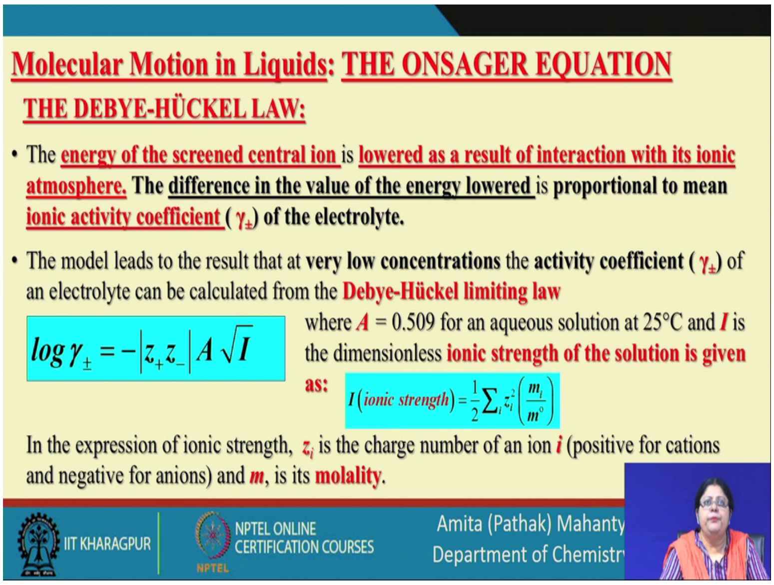

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL LAW:

- The energy of the screened central ion is lowered as a result of interaction with its ionic atmosphere. **The difference in the value of the energy lowered is proportional to mean ionic activity coefficient ($\gamma_{\pm}$) of the electrolyte.**
- The model leads to the result that at **very low concentrations** the **activity coefficient ($\gamma_{\pm}$)** of an electrolyte can be calculated from the **Debye-Hückel limiting law**

$$\log \gamma_{\pm} = -|z_+ z_-| A \sqrt{I}$$

where $A = 0.509$ for an aqueous solution at 25°C and I is the dimensionless **ionic strength of the solution is given as:**

$$I\,(ionic\ strength) = \frac{1}{2}\sum_i z_i^2 \left(\frac{m_i}{m^{\circ}}\right)$$

In the expression of ionic strength, z_i is the charge number of an ion i (positive for cations and negative for anions) and m, is its **molality**.

So, what happens according to Debye Huckel theory what they have found the energy of the screens central ion is lowered as a result of interaction of the ionic atmosphere. You see the if you are looking into the picture you will see; this ion and this ion the columbic interaction between these two ion. This is a positive charge; this is a negative charge, this interaction is going to be affected if you have a shield around it.

So, this haze of the oppositely charged ion across the central ion is actually; shielding this ion from this ion right. End process of shielding what happens the energy of the screened central ion is lowered as a result of introduction of ionic atmosphere. The ionic atmosphere is actually interfering the inter columbic interaction between the positive and the negative ions placed in the solution.

And Debye Huckel theorem sees that if you have if you have a some amount of energy before and then you have some amount of lowering of energy. This difference in energy which is lowered due to the interaction of the ions with the of the ions with the ionic atmosphere. This difference of the energy which is lowered because, of the screening of the central ion by the ionic atmosphere; so, the central ion now if I have; at one point of time where there is no it ionic atmosphere haze around this central ion; that condition and the condition where you have the ionic atmosphere existing.

You will see when it is it was shown that it if you it experimentally it has been shown that you can have a lowering of we have a lowering of the energy of the central ion when they have a at ionic sphere around. So, this difference in energy of the central ion which is lowered this difference in energy was found to be proportional to the ionic activity coefficient of the electrolyte. And according to I am not discussing the Debye Huckel theory in detail, but I am just giving you the gist; so, that we can proceed as to what with the modifications which we have when we have Debye Huckel Onsager equation.

So, the Debye Huckel theorem says that the center line of in ionic electrolyte solution is going to be energy of the central ion is going to be lowered because of the presence of ionic atmosphere. And this lowered energy amount which is lower the difference in the value of the lowered energy is proportional to the ionic activity coefficient of the electrolyte ok.

So, this model led to the result that at very low concentrations of the electrolyte. The activity coefficients the coefficient of the electrolyte can be calculated by the Debye

Huckel limiting law. It is something very beautiful that based on these conditions in physical conditions of physically viewing this as a central ion being screened by the ionic atmosphere. We come up with a beautiful equation which is more or less valid and with whatever we see in experimental results.

So, if in the very dilute conditions of the electrolyte if we have the expression a derived from the Debye Huckel theory, it states that the activation activity coefficient of the electrolyte is going to be proportional to the ionics root over of the ionic strength. So, this is the mean ionic activity coefficient of the electrolyte which we are dealing with. So, if we have something like this; what is happening we are seeing this is the expression which was this is the model try to visualize this. We are trying to we have seen some experimental result, what Debye Huckel was trying to do he was trying to fit a model to x to match whatever experimentally was observed and for that he has given a equation ok.

So, the Debye Huckel limiting law is the equation which we have which he has formulated to explain the behavior of a electrolyte at very dilute conditions. So, if it is a very dilute condition only then these things which we are saying is more relevant. We have the lowering of the energy of the central ion, because of the ionic interaction ionic atmosphere present around them.

Which is screening the neighboring ions in the solution, this lowered amount of energy was proposed to be proportional to the mean ionic activity of the electrolyte. And, that expression was summarized something like this which was a formulation by Debye Huckel. And this was considered to be valid only when very low concentrations of the electrolyte and hence this equation is known as the Debye Huckel limiting law.

So, we have here in this expression this is a constant, this is for a aqueous system at 25 degree we take it as 0.05 0.509. And I is the ionic strength of the solution and how do you calculate the ionic strength of the solution? Ionic strength is nothing, but the summation of the charges z is the charge of the ions which are present suppose I a number of ions are present. The contributions of each ion has in the solution has to be taken. So, the charge square of each of the ions positive or negative ion and multiplied by the molarity of the, here you have not talking about the molarity we are talking about the molality of the solution. That means, 1 kg of the solute in a grams of the solute in 1 kg of the solvent.

So, everywhere you have a expression of mu naught, mu naught is the expression in say for we have some sort of molarity here per kg of the solvent. Here we have 1 gram per kg of the solvent this is this is usually taken to be 1 ok. This is usually taken to be 1 and it is a standard value for when we define usually we do not even write until we have a difference in unit in we are not expressing in molality. Then we can use some other ways of representing mo the mo naught, mo naught is the concentration of 1 gram of the solvent in 1 kg of the 1 gram of the solute in 1 kg of the solvent. So, essentially this is taken to be 1 ok. So, we may ignore it if the as long as the all the equations which we are dealing with is having the same units of molality.

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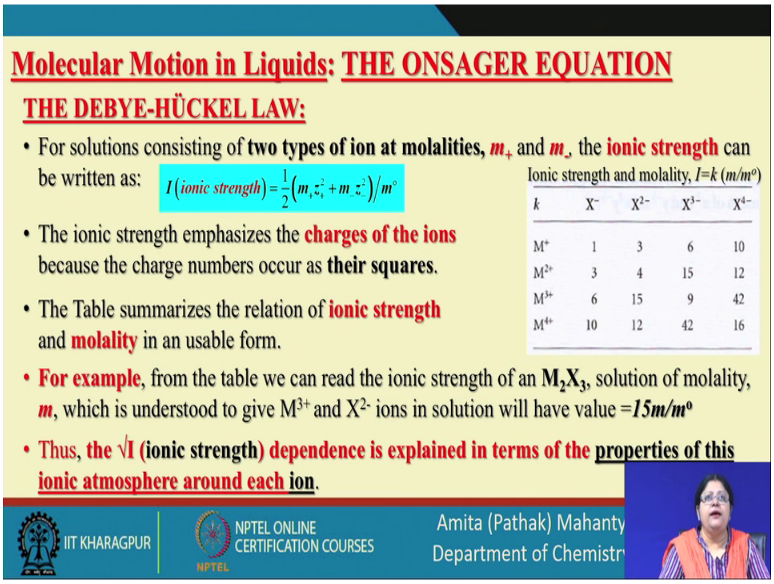

Molecular Motion in Liquids: THE ONSAGER EQUATION

THE DEBYE-HÜCKEL LAW:

- For solutions consisting of **two types of ion at molalities,** m_+ and m_-, the ionic strength can be written as: $I(\text{ionic strength}) = \frac{1}{2}(m_+ z_+^2 + m_- z_-^2)/m^\circ$
- The ionic strength emphasizes the charges of the ions because the charge numbers occur as **their squares**.
- The Table summarizes the relation of ionic strength and molality in an usable form.
- For example, from the table we can read the ionic strength of an M_2X_3, solution of molality, m, which is understood to give M^{3+} and X^{2-} ions in solution will have value $= 15m/m^\circ$
- Thus, the √I (**ionic strength**) dependence is explained in terms of the properties of this ionic atmosphere around each ion.

Ionic strength and molality, $I = k\,(m/m^\circ)$

k	X^-	X^{2-}	X^{3-}	X^{4-}
M^+	1	3	6	10
M^{2+}	3	4	15	12
M^{3+}	6	15	9	42
M^{4+}	10	12	42	16

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So, here what we have? If you have say two different types of ions having each will have a molality of equal M plus will if they are 1 1electrolyte. Then M plus and M minus will be the molalities of each of the ions. And, then the ionic strength will be represented as something as the molality of the plus ion into the charge of the ion which we are talking about. And then the molality of the minus ion into the chance square of the minus ion divided by m naught usually we will take this M naught has to be 1.

So, you see the ionic strength emphasizes the charge of the ions because the charge here is having a square power. So, if we want to find out there is a table which I can show you if we want to find out the ionic strength, the relation between ionic strength and molality of a particulars electrolyte. We can use this sort of a table, see what we have we have the ionic strength and the molality represented as I into K into m by m naught, m naught will take it as 1 ok.

So, suppose we have different type of electrolyte 1 1 electrolyte, this is 1 1 electrolyte. This is the cation which is going to be generated this is the anion which is going to be generated this is the cation which is going to be generated this is going to be the anion which is generated. For example, we take a electrolyte which is M 2 X 3, M 2 X 3 solution molality say let us that the solution molality be m, then what do we have?. So, we have what are the ions which is generated we have M 3 plus and X 2 minus ok. This is going to be the M 3 plus and X 2 minus in the solution.

So, let us see from the table what should be the value I have M 3 and corresponding to the anion will be X 2 minus so this is my factor which I get 15. So, 15 into the molality of the solution which we whichever electrolyte we have, if we know that then we can apply that here and we can find out the ionic strength ok.

So, the ionic strength and the relation between molality can be used to find for various types of electrolyte. What we have in just found out that the ionic strength has a under root of ionic strength dependence can be explained on the properties of the ions surrounding each of the central ion. So, based on this we have we can see that whenever we are having a electrolyte solution if we want to explain how the behavior of the electrolyte in terms of the ionic coefficient mean ionic coefficient. We mean if we know the mean ionic coefficient, we can find out the relationship between the; mean ionic coefficient and ionic strength.

So, the ionic strength dependence instead of we are not talking about the conductivity we had or molar conductivity we are talking about the mean ionic coefficient relationship with the ionic strength. And this was explained by Debye Huckel in terms of the ionic atmosphere in presence of as present; across the central ion. To explain the Kohlrausch’s laws dependence of square root of concentration of the molar conductivity, we can use a similar logic. So, whatever we have whatever was developed by the Debye Huckel theorem could be proposed to be extended to explain the molar conductivity dependence on the concentration in terms of; square root of the concentration, which concentration was in molars moles per liter.

So, this explanation can be; based on whatever we have judged from the explanation for the ionic for electrolyte, where you have ions and that you have a ionic strength dependence or square root of ionic strength dependence in terms of the activity mean activity coefficients of the ion.