Molecules in Motion
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Lecture – 26
Molecular Motion in Liquids (Contd.)

Welcome to another course on molecules another lecture on molecules in motion.

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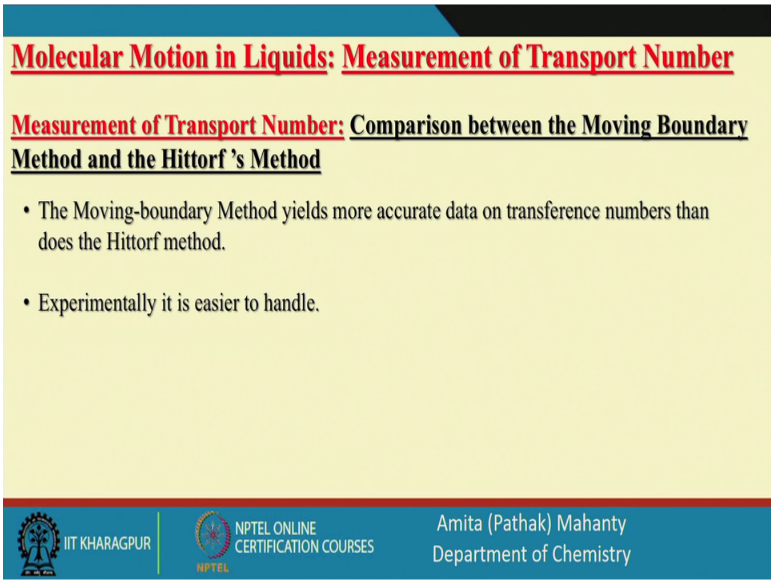

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number: Comparison between the Moving Boundary Method and the Hittorf 's Method

- The Moving-boundary Method yields more accurate data on transference numbers than does the Hittorf method.
- Experimentally it is easier to handle.

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In this lecture, we are going to be discussing some things which probably I have left out in previous discussions, but it is more probably most appropriate to discuss it now. We have discussed the measurement of transport number in the last two lectures and we have introduced two methods of finding out the transport number of electrolyte and that was done through the Moving Boundary Method and Hittorf's Method.

These are two experiments that I have been used to determine the transport number for an electrolyte for a system, where we want to find out what is the portion of the fraction of the current carried out, carried by the anion or the cation when a mole of electricity is passed through the cell. So, what we had? We had talked about the Moving Boundary Method and the Hittorf's Method.

Hittorf Method is one of the oldest methods which is available to us, but it is more of hands on experiments, which we need to do when we are talking about Hittorf's Method and here monitoring of the concentrations of each of the compartment has to be done for each of the electrolytes system and their electrode this combination has to be used for any type of calculations that we want to know or we want to find out. So, we do not have a formula to find out, but we have to understand the electrode reactions, which is happening when the electrolysis happens in a cell.

So, Moving Boundary Method as of now, the Hittorf's Method is sort of a little redundant though it was one of the first pioneering methods put forward to understand that the fraction of current carried by the anion and the cation in that system is always a fraction of the total current which is passed through the cell. So, in the present context the Moving Boundary Method is considered to be more accurate measurement for coining out the transference or the transport number. In addition, the equipment which we have for the Moving Boundary Method is experimentally more easier to handle than the Hittorf's Method.

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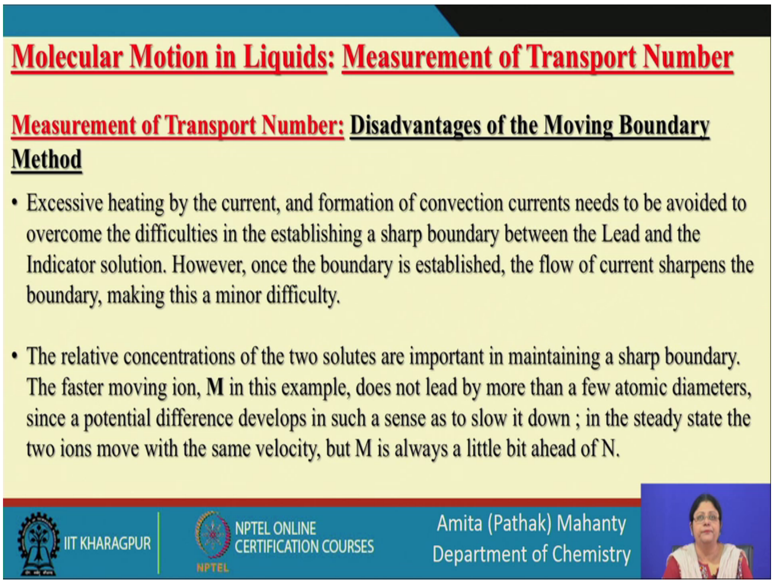

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number: Disadvantages of the Moving Boundary Method

- Excessive heating by the current, and formation of convection currents needs to be avoided to overcome the difficulties in the establishing a sharp boundary between the Lead and the Indicator solution. However, once the boundary is established, the flow of current sharpens the boundary, making this a minor difficulty.
- The relative concentrations of the two solutes are important in maintaining a sharp boundary. The faster moving ion, **M** in this example, does not lead by more than a few atomic diameters, since a potential difference develops in such a sense as to slow it down ; in the steady state the two ions move with the same velocity, but M is always a little bit ahead of N.

Now, saying that, let us see what are the drawbacks or what are the possible disadvantages we have for the Moving Boundary Method what happens we have a when we are sending current through the Moving Boundary apparatus then if you have excess of current, then a there if there is a current which is continuously passed then you may generate a heating associated when passage of current. So, if we have heating, then you have convection currents, generated in the electrolyte system that needs to be avoided to because, you have what you are monitoring here; you are monitoring a sharp boundary between the lead and the indicator solution.

If the lead and the indication indicator solution does not have a sharp boundary generated, then you will have difficulty in reporting the transference number or transport number. So, what we need to take care of conditions which is not going to give rise to diffusion in the sharp boundary between the lead and the indicator solution. So, what we need to avoid; we need to avoid the heating associated with the passage of current which may generate convection currents which can give rise to diffusion in the sharp boundaries.

However, the method is, once it is established the flow of current sharpens the boundary and makes the minor difficulty can be overcome, then another point which needs to be taken into account when you are talking about the moving boundary the relative concentration of the two electrolytes needs to be maintained which is required for a sharp boundary. If you have a fast-moving ion, for example, m in the discussion which we had, does not lead to any by say it does not lead by more than a few atomic diameters, since, the potential difference develops in such a sense to show slow it down.

In the steady state the ion the two ions will have the same velocity, but the m ion will be always a little bit ahead of n. So, what we have to understand, the relative concentrations of the two electrolytes have to be maintained such that the main boundary of the two solutions are sharp, because eventually that difference is only of the which because fast-moving ions may be whatever, maybe they are moving faster or slower the difference in the lead solution and the indicator solution is probably in the order of few atomic diameters too. So, to have them very clearly generated, what you need to know; we need to maintain a condition where the relative concentrations are appropriate in the lead and the indicator solution. Now, saying that, those are the main two disadvantages in the Moving Boundary Method.

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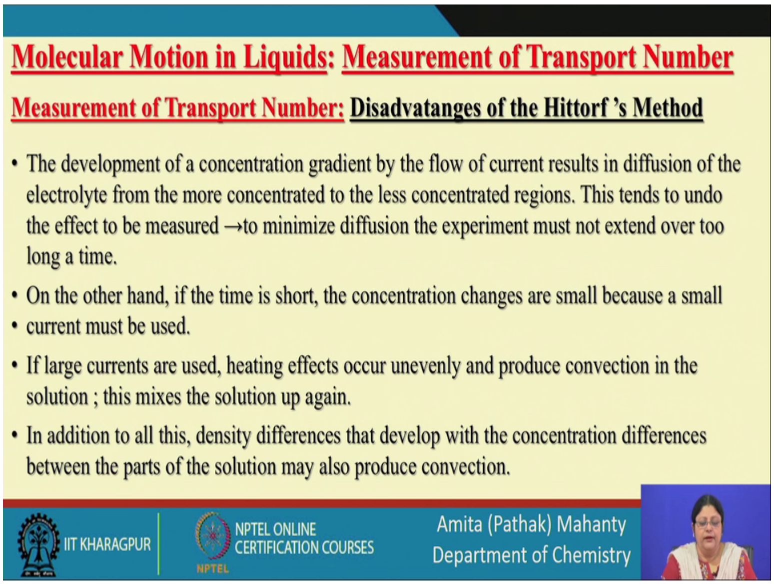

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number: Disadvatanges of the Hittorf 's Method

- The development of a concentration gradient by the flow of current results in diffusion of the electrolyte from the more concentrated to the less concentrated regions. This tends to undo the effect to be measured →to minimize diffusion the experiment must not extend over too long a time.
- On the other hand, if the time is short, the concentration changes are small because a small
- current must be used.
- If large currents are used, heating effects occur unevenly and produce convection in the solution ; this mixes the solution up again.
- In addition to all this, density differences that develop with the concentration differences between the parts of the solution may also produce convection.

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Now, what are the disadvantages of in the a moving boundary method now what is the disadvantages of Hittorf, if I keep listing of them, then you probably will think Hittorf is one of the; obviously, not preferred method, but believe me experiment wise Hittorf's Method can be done in the lab much more easily.

So, what happens in a Hittorf Method, the concentration gradient by flow of current results in the diffusion of the electrolytes from more concentration or less concentration region. This leads to the to undo the effects to be measured to minimize this diffusion, the experiment must be not extended over too long a time; understood what I am trying to do? Here we are having the electron move because of this is not diffusion control. You are having the cations, moving to the negative electrodes and here movement of the ions is driven by the potential difference. Ok? It is not diffusion control process.

But if you have too much concentration gradient, if you see what happens in that you have accumulation of the copper to ion, in the last lecture we had seen and the copper to ions get accumulated in the cathode compartment. The concentration of the ani[on]-cation plus two copper is increasing and here in the anode compartment, you have a some of amount of copper, dissolution of copper from the electrode to the solution is taking place.

So, if you have accumulation of the charges, accumulation of the cations in any of the compartment what will result, we have a diffusion of the electrolytes, the ions [sat/start] starts moving due to difference in the concentration because, if you have a concentration then you will have a gradient in concentration and that will drive for the ions to move from a more concentrated to a less concentrated region and not entirely guided by the difference in potential with across the two electrodes.

So to avoid this, what we have to do? We wecannot make the experiment too long. So, that if you are extending the experiment for too long then you have tended to see those effects more prominently. So, again if the time is too short the concentration changes as too small and the current cannot be measured. Small amount cannot be used to determine the results.

So, because we are talking about the moles of this cation and anion changing in the each compartment until you have sufficient amount of electricity passing, then until that is done you cannot change see the change, note the change, because the changes are going to be very small.

So, what we have to do; we have to have an optimized amount of time spent for the current to pass electricity. So, that we have sufficient amount to judge the concentration change and not excess. So, that we have diffusion control current generated in the system. If large currents are used heating effects occurs unevenly and produce convection in the solution, this mixes up the solution again. So, like in Moving Boundary Method here also we have to see that the large amount of currents which is used, does not cause heating effect.

If you have heating effect then you have a convection current and uneven current is accumulation of ions is going to take place and this is going to give rise to the interference in the cell. In addition to this in the density difference that develops with the concentration difference between the parts of the solution may be may also produce convection. So, density difference means the concentration difference which is going to be arisen in the different parts, is also going to give rise to the diffusion control current.

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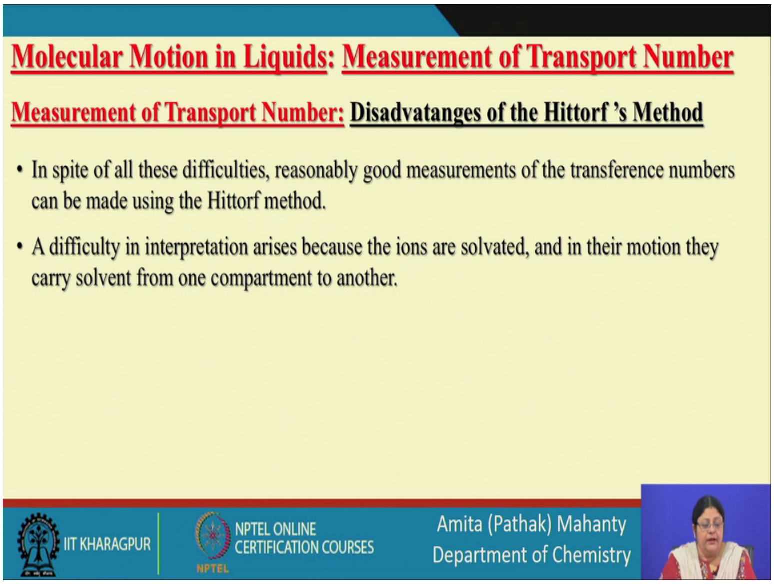

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number: Disadvatanges of the Hittorf 's Method

- In spite of all these difficulties, reasonably good measurements of the transference numbers can be made using the Hittorf method.
- A difficulty in interpretation arises because the ions are solvated, and in their motion they carry solvent from one compartment to another.

In spite of all of these difficulties a reasonable good amount of measurements of the transference number can be done by the Hittorf's Method and difficulty in interpretation arises, because E ions are all solvated and their mobilities and their motions and in their motion they carry solvent from one compartment to the other. So, if you are going to go into a very detailed interpretation of what you are going to see then you have to take the solvent affect the ions are actually solvated when we are having in the motion.

Now, when we talk about the solvated ion what I have we missed out in previous classes is to let you know about the Walden’s rule. What is the Walden's rule?

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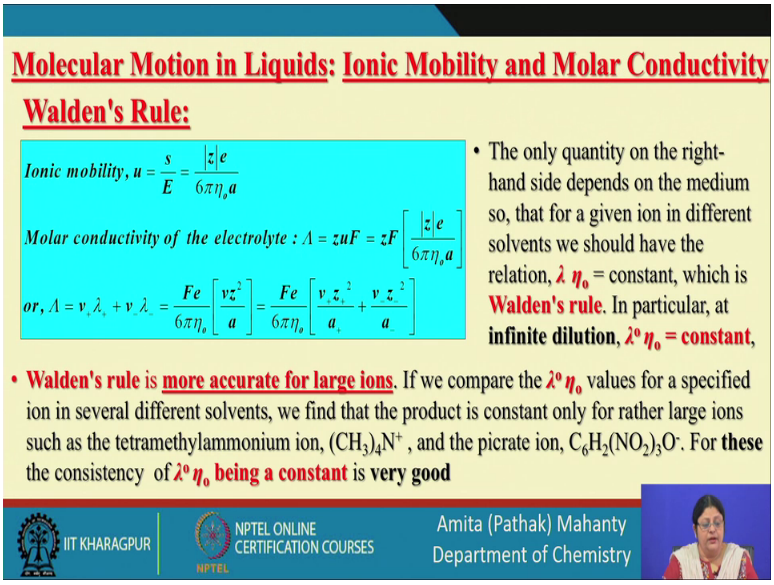

Molecular Motion in Liquids: Ionic Mobility and Molar Conductivity

Walden's Rule:

$$\text{Ionic mobility, } u = \frac{s}{E} = \frac{|z|e}{6\pi\eta_o a}$$

$$\text{Molar conductivity of the electrolyte : } \Lambda = zuF = zF\left[\frac{|z|e}{6\pi\eta_o a}\right]$$

$$\text{or, } \Lambda = v_+\lambda_+ + v_-\lambda_- = \frac{Fe}{6\pi\eta_o}\left[\frac{vz^2}{a}\right] = \frac{Fe}{6\pi\eta_o}\left[\frac{v_+z_+^2}{a_+} + \frac{v_-z_-^2}{a_-}\right]$$

- The only quantity on the right-hand side depends on the medium so, that for a given ion in different solvents we should have the relation, $\lambda\,\eta_0$ = constant, which is **Walden's rule**. In particular, at **infinite dilution, $\lambda^o\,\eta_0$ = constant**,
- **Walden's rule** is **more accurate for large ions**. If we compare the $\lambda^o\,\eta_0$ values for a specified ion in several different solvents, we find that the product is constant only for rather large ions such as the tetramethylammonium ion, $(CH_3)_4N^+$, and the picrate ion, $C_6H_2(NO_2)_3O^-$. For **these** the consistency of $\lambda^o\,\eta_0$ **being a constant** is **very good**

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Walden's rule, if you see the ionic mobility definition, it is the drift speed by the applied electric current and from the derivation which we had used stokes to use stokes law and from there we had found out this expression of the ionic mobility and the ionic a molar ionic conductivity of the electrolyte was capital lambda which was nothing, but the zu F z is the charge of the electrolyte, u is the ionic mobility, F is the faraday constant if you apply the value of u here from the expression, then you get something like this, but we know, if we want to find out the molar conductivity of the electrolyte.

It is nothing, but the sum of the conductivities of the individual cation and the anion and this should be multiplied by the formula unit amount of the cation generated for the each type of electrolyte plus and minus. So, if I can rewrite this, if you can see this you can take the takeout the common part which is get going to be varying for a given solvent system. What is going to be same? This is the eta, it is eta; eta is the viscosity of the solvent system and z is the charge of the electrolyte, e is the charge of the electronic charge, a is the say the diameter of the cation or anion, which we are looking into.

So, if I can separate them out as to which are things, if for a common solvent system what can happen faraday into e is the electronic charge that remains constant 6 pi into eta; eta is the solvent system if I can separate that out then this can be represented something like this, like if you have the contributions of the cation, then that amounts of the number of moles, a number of cations generated per formula unit of the electrolyte that into the charge of charge square of the electrolyte divided by the diameter, lambda, diameter of the anion.

So, similarly for the cation and similarly, for the anion can be separated out by virtue of this. Only thing what we have seen is, there is a square term of the z in if you compare these two. So, when you are having this the only quantity on the right-hand side depends on the medium. So, for a given ion in different solvent we can write this is a constant lambda into naught is a constant which is the Walden's rule. If we want to find out for an infinite dilution where the concentrations are very low, then we can say the molar conductance of the at infinite dilution into the viscosity of the solvent should be a constant.

So, what we have come out? We come out with a fact that lambda into the viscosity coefficient of the solvent system, if we multiply, then it should be a constant. So, which side is the side, which is dependent on the solvent system? So, from for a given's ion in different solvents what we can have if we have for a given ion in different solvent the ions are the same, the diff solvents are if the solvents are different then we can say that it is nothing because this is this is going to be lambda. What is the lambda? This is the lambda, this is the lambda.

So, lambda expressions, if you can see lambda expressions is this is the lambda. So, this is entirely going to this is the lambda part and if the amount of this is changed, then what you get if this is going to be fixed, then what you can get is lambda into eta naught is a constant for a system will depend on the medium. So, if you have different mediums you will have different values of eta naught. So, eta naught into this is the solvent viscosity coefficient into the ionic mobility of the electrolyte system should be a constant.

So, for infinite dilution we can represent this by the alpha naught value lambda naught value into the coefficient of viscosity of the solvent to be a constant the Walden's rule is more accurate for large ions, if we compare the lambda naught into the eta naught value for a specific specified ion in different solvent we will find, we use different solvents and we are comparing the lambda naught into eta naught values for us a specified type of ions for separate several different solvent.

We will find that the, this product is a constant only for a large ion such as tetramethyl, ammonium ion, picrate acid, for these the consistency of this being a constant is very good. What we are looking into? We are trying to see the Walden's rule, where which states the product of the lambda, which is the ionic conductivity molar ionic conductivity at infinite dilution into the viscosity coefficient of the solvent is constant, if we want to compare that for a very large=, ion then what we can do?

We take the specified ion in several different solvents and we see what is the product of lambda naught into the eta naught and the product for a very large number ion such as the tetra ammonium ion. This is a quaternary salt and the picric, picric ion, picrate ion. These are very large ions, for these it has been found that the consistency of the product being a constant, this product being constant is pretty good.

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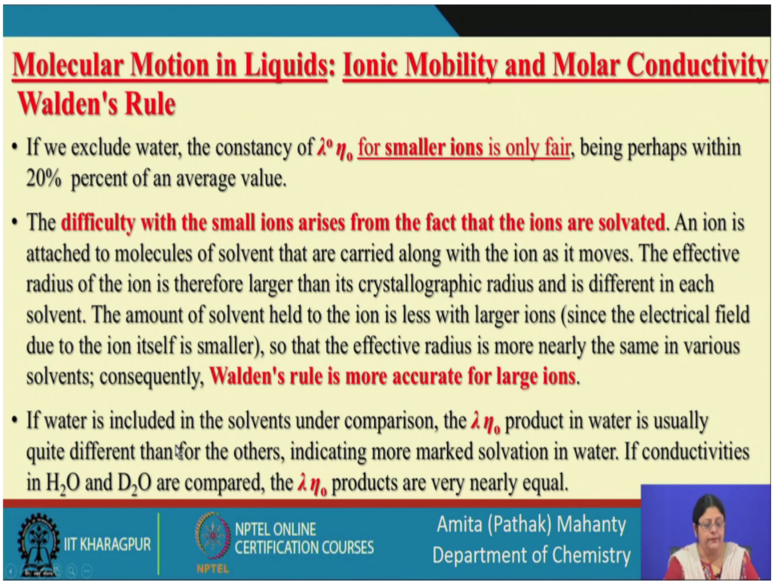

Molecular Motion in Liquids: Ionic Mobility and Molar Conductivity

Walden's Rule

- If we exclude water, the constancy of $\lambda^{o}\eta_0$ for smaller ions is only fair, being perhaps within 20% percent of an average value.
- The **difficulty with the small ions arises from the fact that the ions are solvated**. An ion is attached to molecules of solvent that are carried along with the ion as it moves. The effective radius of the ion is therefore larger than its crystallographic radius and is different in each solvent. The amount of solvent held to the ion is less with larger ions (since the electrical field due to the ion itself is smaller), so that the effective radius is more nearly the same in various solvents; consequently, **Walden's rule is more accurate for large ions**.
- If water is included in the solvents under comparison, the $\lambda\eta_0$ product in water is usually quite different than for the others, indicating more marked solvation in water. If conductivities in H_2O and D_2O are compared, the $\lambda\eta_0$ products are very nearly equal.

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If we exclude water, if we do not say take water as the solvent, then the consistency of this product for electrolyte system is also fairly good for a small ion ok. So, if I say, if we do not use water as the solvent medium then the product of the lambda that is molar ionic conductivity at infinite dilution into the solvent viscosity for a small ion is also fairly consistent perhaps, within 20 percent of the average values.

The difficulty in the small ions arise from the fact that ions are solvated and ion is attached to the molecule of molecules of the solvent that I carried along with the ions as they move through the medium on the, when on the passage of electricity the effective radius of the ion is therefore, larger than that the crystallographic radius, that you can find for the cation or anion and in diff, it is different for each type of solvent.

The amount of solvent molecules that is held to the ion, the amount of solvent held to the ion is less with larger ions since, the electric field due to the ions itself is small. So, the effective radius is more nearly the same of the various in various solvents. So, Walden's, Walden's rule is more accurate for large ions and for systems, which is, not water as a solvent.

What happens if you have a large small ion, the small ions will have a higher charge, density on sitting on them. If they are having larger charge density as they move through words, the through the solution on the under the influence of electric field then, because of their charge density being higher on them they tend to carry more number of solvent molecules along with them. When they are passing through the solution and if that carrying more amounts of solvent molecules with them then these are the solvated ions.

The radius of the solvented ions is; obviously, going to be large much larger, when the ions are smaller, because of the charge density sitting on a small ion ok. So, the effective radius of the ions will be the therefore, much larger than whatever they expected crystallographic radius, which we have reported in the books is going to be much, compared to the, crystallographic radius.

It is going to be much higher, because now, we are dealing with the solvent, solvated molecule, where the ion is actually in having a sphere in which, sphere around it, where you have the molecules of solvent at associated with the cat, anion or cation, which we are which is moving. So, the effective radius is, nearly more when, to the say to that of whatever we have, obtained in a crystallographic, measurement will be more close to that of for, on which is of larger size and hence Walden's rule will be more accurate for the ions, which are larger.

Now, if water is included as the solvent under comparison then what happens? The product of the molar ionic, molar conductivity into the, solvent viscosity coefficient is usually quite different from others indicating a more marked solvent, salvation in water ok. If conductivities into water and when H 2 and D 2 are compared, then what happens? The lambda naught into the lambda into the eta naught the solvent viscosity product is nearly equal. So, what does that mean if water is included in the solvent under comparison?

This product is the product of ionic conductivity into the viscosity coefficient in water is usually quite different from the others indicating mores marked salvation in water ok. If I have compared to two types of solvents and if we want to measure the conductivities and take into account their viscosity coefficient of the solvent, if water is included as the solvent and the comparison, the product of the, lambda and eta naught is usually quite different from that of the other solvents, but if you have conduct with conductivities, say in water and D 2 O compared then the lambda into eta naught; that means, the coefficient viscosity of the products are nearly equal.

So, what we have here discussed is the Walden's rule. Now, we are going to in the next class discuss, how the concentration variation of, when we are talking about molar concentration, molar conductivity. How this molar conductivity is dependent on the, concentration of the electrolyte, if you remember, according to Kohlrausch's law, it is going to be dependent on the under root or square root of the molar concentration.

So, in the next class, we are going to discuss what is the reason to have the conductivity or the molar conductance of electrolyte having a dependence of under roots molar. When the square root of concentration of the electrolyte in terms of molar concentration, why is it depend on under root C? Why is the, molar conductivity or conductivity depend on under root C, where C is the molar concentration of the electrolyte.

This is going to, what we are going to, establish using the Onsager and put forward the Onsager equation, which is the modified equation, when we take into account, what are the other contributions and majorly there are two types of contributions, which is going to retard the motion of the ions through the solution. So, instead of having ions moving through the solution, we have the, here we have the ionic conductivities proportional to the, under root of the concentration of the solvated ion. So, this relationship we will take up in the next class.

Thank you.