Molecules in Motion
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Lecture - 34
Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules in Motion. In the last class, what we were talking about was the Einstein's relationship, where we had what we are essentially talking about, we are talking about migration of particles through a medium and the depending on what type of thermodynamic force, which is going to guide them, we are going to get a expression. What we had tried to link last time was through Einstein relationship, we had tried to get the expression or link relationship between ionic mobility and the diffusion coefficient of a particular ion or particle.

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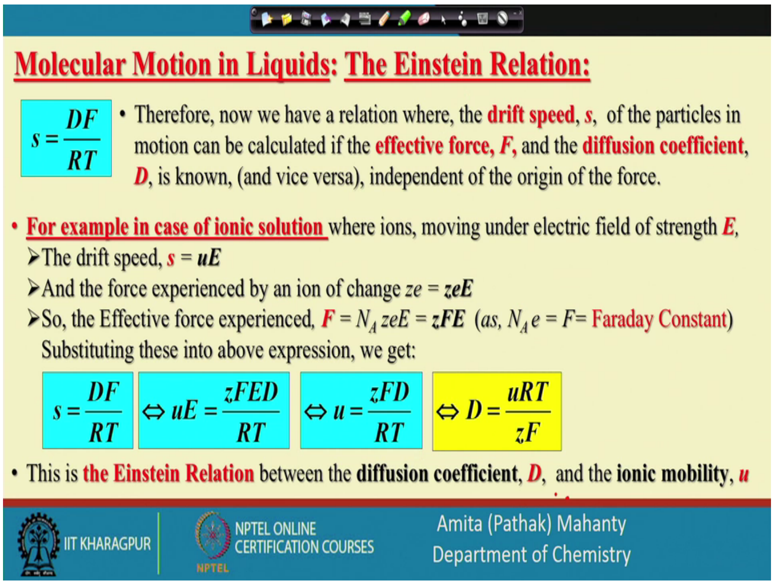

So, if we are looking into that, this is what we had done in the last class. So, since I am going to be doing modifications of this relationship, so let us revisit what it was. So, the Einstein's relationship what we had established from the fact that the drift speed of a particle s is equal to the ratio of capital D the diffusion coefficient of that particular particle into the thermodynamic force divided by RT.

So, at a given temperature and pressure what we had found, that if we know the drift speed and when do we get the drift speed possible, when we have the thermodynamic force balanced by the viscous force of the medium. So, when we if that was the condition we had said, it is independent of the origin of the force, this is going to be valid, where the speed of the particle the drift speed is equal to the ratio of the diffusion coefficient into the driving force divided by thermodynamic force divided by RT. So, this is the effective force or the thermodynamic force, which is giving rise to the motion of the particles in the medium by virtue of which we are getting the motion of the particles in this medium.

We had taken a particular example for of ionic solution, where the ions are moving under a electric field. If the ions are moving under a electric field, we have initially derived that the speed drift speed will be equal to mobility into the strength of the electric field E, this was the expression we had right. So, what was the force experienced, what is the supposed to be the force the particles are going to be experiencing. If that if they are charged particles, then the each charge is going to be ze and each charge is going to experience ze into the field strength of the applied field strength as the force, which is going to be experienced by a single ion.

So, the effective force for the particles or the ions in the electric field strength of E will be nothing but Avogadro number into ze into capital E, this capital is the field strength. So, what we had derived was the effective force, the force the thermodynamic force, which was driving the motion of the particles was nothing but equal to z into the faraday constant into the electrics the field strength, which we are talking about.

Now, from these two expressions of the s this is the s, we had derived in the beginning of the Einstein equation. So, this s and the s, we have here. If you see the two relationship, then we can say uE will be equal to DF by RT, because both are s, so they can be equated. So, uE equal to DF RT. And what is the F; this is the effective total effect force in the system. And the total effective force in the system, we have derived this is equal to z into faraday constant into the electric field strength ok. So, substituting this in place of F here, we get D into zFE. We are placing this F by zFE. So, zFE into D by RT should be equal to u into E. Now, we cancel of this E in both the sides with the field strength remaining same. So, what we have, we have a relationship between the mobility of the ion in terms of the diffusion coefficient.

And this diffusion coefficient can be if you rearrange, you will get the diffusion coefficient is nothing but RT into u by F that is the faraday constant. So, we have a relationship, we have a link between [nailing/ionic] mobility and the diffusion coefficient. So, if we know the ionic mobility, we can find out the diffusion coefficient for a particular ionic system.

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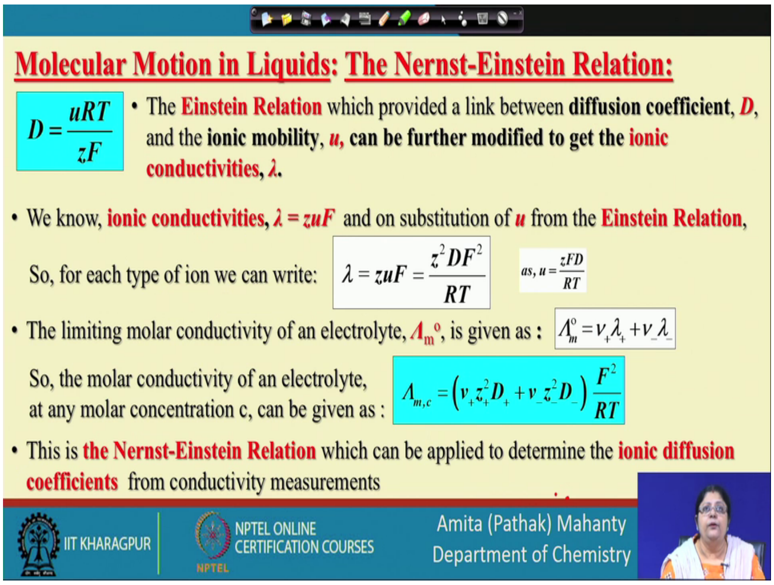

Now, this is that was the basis that was the Einstein relationship. Now, the Einstein relationship between the diffusion coefficient and the ionic mobility can be further modified to get the ionic conductivities. So, if you remember the ionic conductivities, what was ionic conductivity, this is what we have this is the Einstein relationship. So, in this expression, we have the mobility uRT and this is the faraday constant.

We know that the ionic conductivities can be expressed ionic conductivity expresses lambda is equal to zuF. I hope you remember this; we have derived this in previous classes. So, the ionic mobility lambda is equal to zuF, where u is the ionic mobility. So, if you substitute the u, which you have from the Einstein relationship what is the u here, you see u will be equal to zF into D divided by RT right, u will be zF zFD divided by RT right.

So, zFD divided by RT if you substitute that value of u in this expression for ionic mobility, what do you get, z is already there, F is already there, now you are substituting for u and what is the u you have got, zFD by RT ok. So, substituting this what do you have, you have the z square D into F square by RT right. F is the faraday constant and RT is the whatever temperature and R is the gas constant, whatever the temperature is corresponding to that, we are going to take a condition aware, we are talking about having the experiment done at a given temperature and pressure.

So, the limiting condition of the conductivity of a electrolyte is given by lambda m naught, which is going to be what we are talking about independent migration of ions. So, the molar conductivity and limiting conditions of infinite dilution what you have, this is the stoichiometric constant for per molar molecular formula of the electrolyte of the plus ion generated into the molar ionic mobility of the positive charge into a plus the in the stoichiometric coefficient of the per formula unit of the molecule, the number of anions generated.

So, number of anions generated per formula unit is nu minus and number of cations generated per formula unit is the nu plus. So, nu plus into the ionic mobility of the cation plus the nu minus of the ion into the ionic mobility of the anion. This is what according to the (Refer Time: 09:47) law, we have derived.

So, if this is the condition, then for molar conductivity of electrolyte at any concentration what we have to do? We have to now substitute the values of lambda in this expression and find out what will be the relationship between the lambda and the diffusion coefficient. So, if you can rewrite this, for each of the ion the ion will have different cation will have a different mobility a diffusion coefficient and anion will be having a different diffusion coefficient. So, what we can rewrite, this expression we are how are we getting that, we are rewriting that in terms of the lambda and where lambda is associated with the cation and the anion independently.

So, what we have for each of the ions in this expression in this expression, what we have taken out, this is going to be different for a cation, this is going to be different for anion. So, this is going to be dependent on the type of ions, we are getting in the system. Diffusion coefficients also going to depend on the type of cation or anion, we are involved with, R is a constant gas constant, T is the temperature and F is also a constant that is the faraday constant.

So, these constants I keep aside these constants I keep aside, so that becomes the lambda becomes the capital lambda for the electrolyte for at any concentration c becomes mu into lambda plus. And lambda plus is going to be corresponding to z plus and D D plus into the nu plus. Plus for the anion z minus that will be squared D minus into the nu, understood. What we are doing, we are substituting here in place of lambda, we are substituting that for the capital lambda, which is nothing but the summation of the cations and anions in the system.

So, cation and the number of cations generated per formula unit is nu plus and number of anions generated a for formula unit of the electrolyte is going to be a nu minus. So, nu minus into lambda, you have the lambda expression here already. So, you just need to multiply that with the nu and also associate the discriminate between the plus and the minus, all the rest will be just a constant, this part is going to remain constant. So, D, z and nu are what is going to change for each of the cation and anion.

So, this relation what we have, where the molar conductivity of an electrolyte of concentration c, can be determined in from the expression given as this, where nu plus into z plus square into D plus the diffusion coefficient of the cation plus nu minus z square, nu is the number of anions generated per formula unit and z square is the charge for the anion and D minus is the diffusion coefficient of the anion. This relationship is known as the Nernst-Einstein relationship. And you see, you can find out the diffusion coefficients from conductivity measurements through this expression.

So, diffusion coefficient for the cation and anion can be carried measured experimentally through conductivity studies. So, this is a very important relationship and we call this as the that Nernst-Einstein relationship, which is going to relate the diffusion coefficients of the individual ions to the ionic conductivities of each of the cation and anion right.

So, when we are talking about cation and anion, we cannot find that out separately, but what we can find out through conductivity measurement is the total u a total lambda. This is the for the for the electrolyte, this for a electrolyte can be found out from the conductivity studies. So, if I know this, then I can find out and what are the charges if I know, what is the formula of the electrolyte we know, then we know what is the number of cation and anion generated. So, I can generate an equation, where I can I have the expression of diffusion coefficient for the cation and anion and I can do various conductivity studies to find out the values of D plus or D minus.

The lambda, which we are talking here is the lambda of the electrolyte, which is composed of the cation and anion. And this is what you measure, when you are doing the experiment ok. Whatever the experiment you have a conductor meter. Whenever you are doing the conductor metric studies, you have prepared a solution. Now, the conductor metric studies will give you some value of the lambda and that lambda is what you are going to put here. So, we have a relationship or link between the diffusion coefficient of the ions to that of the molar ionic conductivity of the electrolyte right.

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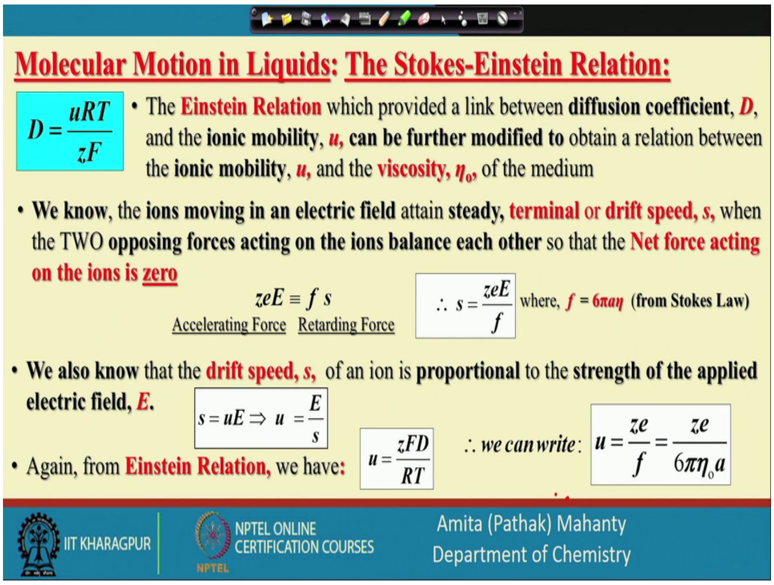

Now, we have another relationship, which is fully important and significant, starting from the Einstein relationship. Einstein relationship is the one, which is marked in blue, where you have the diffusion coefficient D related to the ionic mobility. We further modify this equation in terms to get relationship link between the diffusion coefficient and the viscosity of the medium.

So, if we are talking about viscosity of the medium, again let us talk about a case, where I have ions moving under the electric field. When does the ion attend the terminal velocity or the drift speed that is a speed, which is through which it is going to be constant; when the opposing forces and the opposing forces that is the accelerating force as well as the retarding forces are balanced so that the effective force on the particle, which is moving under the electric field is 0.

When is that going to happen? That is going to happen, when the effective force this is the effective force, which is existing on a particle, ze is the total charge into the electric field is the total. What is the force which is the particle or the ion is experiencing? One ion is experiencing under electric field. This is going to accelerate the particle to move forward, because the charged particles when under a field, they will try to move toward the respective electrode, the positive will try to move towards the negative electrode and the vice versa.

So, what we are looking into, the accelerating force is on a particle is the charge of the particles ze into the field strength capital E and that is supposed to be balanced by the viscous force, which is associated with the medium F into s. The retarding force acting on the particle because of the viscosity of the medium or viscous drag has to be balanced by the accelerating force only, then the particles will move with the steady speed known as the drift speed or terminal speed.

So, from here what you have from here what you have is this the speed drift speed is nothing but ze into capital E by F. What is this F, this is the this entire thing is the frictional force and this is the electric force which is operating on one particle. So, we need to multiply with this Avogadro number to get the total force right. So, N A into ze f will be the total force equal to the F factor into the speed, which is the viscous force.

So, the frictional force is balanced by the electric force and then we can rewrite this in terms of s being equal to ze into capital feed strength divided by F, where what is F, it F is what we get from Stokes Law 6 pi a into eta naught. Eta naught is the viscosity of the medium in which we are having the particles moving. Now, this is what we get from the expression of balancing of a force. Remember, we need to multiply with a to get the effective force, we need to multiply this with a Avogadro number ze small e into capital E the field strength into the Avogadro number by f will be the speed of the total particles moving.

Similarly, we have seen that the drift speed is equal to the mobility into the electric field ok. So, the mobility is nothing but u equal to E by s right. And what is s; s is ze capital E into Avogadro number divided by f f small f; and small f is this ok. Now, we have two expressions of u; one is from the expression z equal to ionic mobility into the field strength and another one is the s, where ze is the charge of the particle into the field strength into Avogadro number by f ok.

So, if I have these two expressions of s, from here we have an another expression of u, sorry we can we talk in terms of the u, because we are going to be using the Einstein's relationship. So, Einstein's relationship from Einstein's relationship we know that, u will be the mobility will be nothing but z into F into D divided by RT right. And from this expression from this expression, where the u will be equal to E by s, where s is this factor, there will be an Avogadro number here as charge into the electric field into Avogadro number by f.

So, we can rewrite this that we can rewrite u as we can rewrite u as ze into Avogadro number by f right ze into Avogadro number by if you can substitute the value of f, this is the value of f. So, now what we have? We have two expression; one of u, one is from here u equal to z small z into e that is the total charge into the total number of Avogadro number of particles N A divided by 6 pi eta a ok, this is one expression of u. And another expression of u, we have from the Einstein relationship from this expression right.

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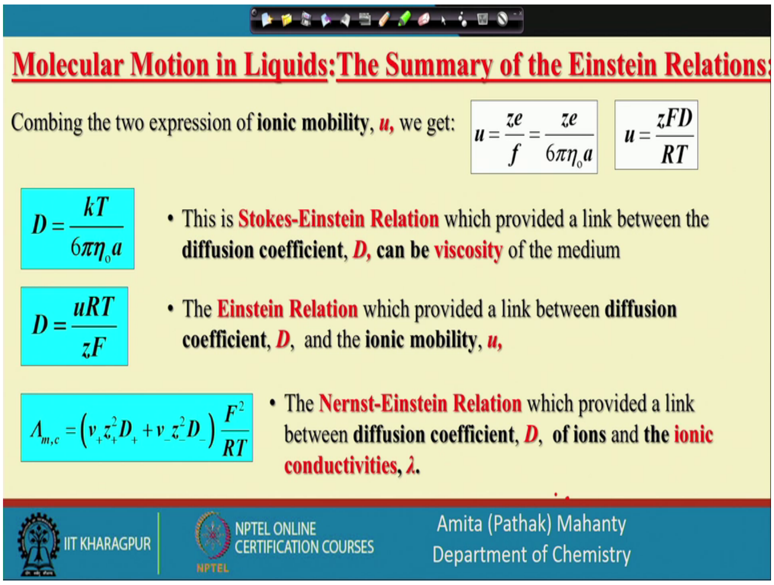

Now, if we compare now if we compare and combine the two expressions, please put a Avogadro number here put the Avogadro number here. So, what you have, you have two expressions of u and we are combining them together. What I have, I have ze into

Avogadro number divided by 6 pi eta naught into a the radius of the charged particle equal to small z into faraday constant divided by a multiplied by D RT.

Now, if I want to find out u the diffusion coefficient D, I have to equate this part to this part what happens, z gets cancelled ok, faraday is nothing but the electronic charge into Avogadro number. So, you have e into N A e into N A, e will also get cancelled, so you have N A by R N A by R can be replaced by k the Boltzmann constant. So, you can rewrite Boltzmann constant into T divide by 6 pi eta naught a will be equal to the diffusion constant.

So, what we have, we have the Stokes-Einstein relationship in which we have a relationship between the diffusion coefficient D and the viscosity coefficient of the medium. So, eta naught is the viscosity coefficient of the medium ok. So, we have now derived three expressions, for finding out the linking the diffusion coefficients with one is the mobility ionic mobility that is the first equation, which we had that is the Einstein relationship.

We modified that with a charge particle moving under electric field, to get the relationship between the ionic the diffusion coefficients of the ions with that of the ionic conductivities, lambda and that was called as the Nernst-Einstein relationship. And then finally, we derived what is known as the Stokes-Einstein relationship in which we had a link between the diffusion coefficient of a medium and the viscosity coefficient of the solvent or medium in which we are having the electrolyte or any particle.

So, these general equations to in general equations and for this charge particle are very important equations to relate a diffusion coefficient. Diffusion means, why is it important, why diffusion is coefficient is important. Diffusion means, we are talking about migration of a particle. So, a diffusion means, when a particle is moving from one medium from a concentration gradient as a driving phase force or other sources of force. Depending on that depending on the type of force, we have effective force, which is applicable, which is the thermodynamic force driving the flow of the particle through a medium.

We have generated three equations relating the diffusion coefficients with the various measurable parameters like viscosity, ionic mobility and ionic conductivity. So, through experiment, we can find out the diffusion coefficient. And if you know the diffusion coefficient, you know the how on the rate at which the particles are moving through a medium, whether in presence of electric field or in absence of it. These are general equations, which can be applied to particles, which may not be charged.

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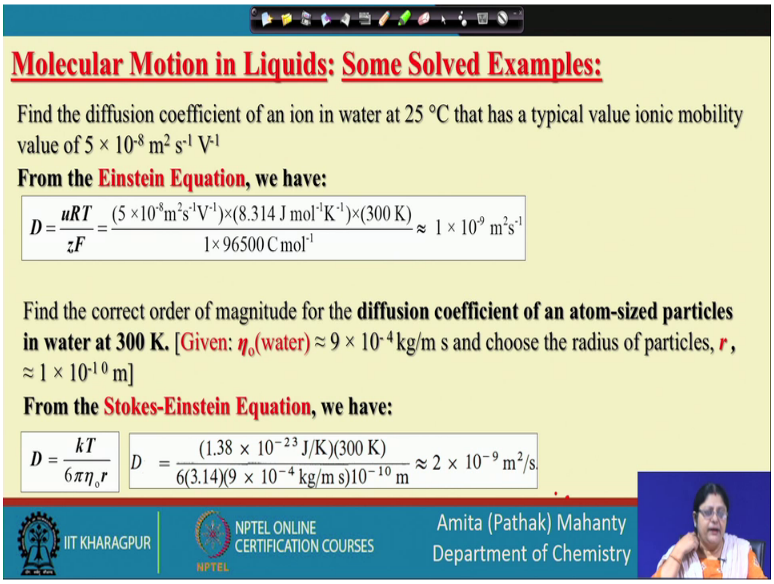

So, this, I will end this lecture with a small solved example using the Einstein relationship and Stokes-Einstein relationship. So, both of these its examples are actually this more or less same, you will see what I am looking at find the diffusion coefficient of ion. We have find the diffusion coefficient of ion in water at 25 degree that has a typical ionic mobility value of 10 into 10 to the power minus 8 meter squares and second inverse per volts ok.

So, what is the relationship what is the equation we are going to use, since the ionic mobility is given, we are going to use the Einstein's relationship. What is the Einstein relationship, the diffusion coefficient is equal to the ionic mobility into R into T divided by zF. So, F is the faraday constant. So, you put the value of faraday constant here, which is supposed to be a given constant, you should be knowing.

Now, you assume that the ion, which is moving is a univalent ion. So, if there is not mentioned that what is the charge of the ion, you take it the charge to be 1, so the charge is 1. And u is the mobility, which is given to you. This is the u, which is given to you into R, which is the gas constant; we will take it in joules per mole per kelvin.

And what is the temperature, 25 degrees is the temperature ok. So, the temperature sorry it should not be and this should be 27 degree, I have taken 300. So, this should be 27 degrees at that temperature will be converted to kelvin, so 27 plus 273 is 300, so 300 kelvin. So, it is going to be approximately around 10 to the power minus 9 meter square per second ok. This is the diffusion of a single ion a univalent ion through a medium water at 27 degree centigrade.

Now, again another question which I have written down numerical;, find the correct order of the diffusion coefficient of an atom-size particle atom-size particle in water at 300 K. And the eta value for water is given to you. So, if eta value is given to you, which should be the equation you are supposed to use, you are supposed to use the Stokes-Einstein equation. Stokes-Einstein relationship is the diffusion coefficient equal to Boltzmann constant into temperature divided by 6 pi eta naught r or a. Here r is the radius of the particle.

And choosing that atomic size particle, we take the order of the particle to be 10 to the power minus 10 meters, because usually the atom-size is in the order of 10 to the power minus 10 meters. So, whenever we are giving this as a hint atom-size particle, you are only going to be giving me a order magnitude, I am not asking exactly exact value. So, when I am approximating the atom-size that means, I am going to be taking it the value to be 10 to power minus 10 meters right.

So, what we have substituted here, we have substituted the Boltzmann constant, the temperature 300 kelvin into 6 pi is 3.14 into the viscosity of water. Viscosity of water is given to be 9 into 10 to the power minus 4 kg per meter second. And r is what, the radius of the particle, which I have taken to be of the order of atom, which is 10 to the power minus 10. If you solve that, what you get is 2 to the power minus 9 meter square per second.

So, you see at the same temperature the order of the particles, I have calculated through one through the Einstein equation and other through the Stokes-Einstein equation, the order is remaining the same ok. So, the both the expressions are almost correct, but you are supposed to know which equation to use, when you are dealing with ionic mobility or we are doing dealing with viscosity of the medium right. Please practice few problems on these three expressions which we have derived Einstein relationship, Stokes-Einstein relationship and the Nernst-Einstein relationship.

One of the major things are what are the values on which we can determine the diffusion coefficients? Diffusion coefficient becomes important, because that is going to give you the rate at which a particle is going to diffuse through a medium. So, how they are propagating through a medium is for or various applications you need to know, how the particles are moving in the medium, so that you can formulate expressions or do calculations or do applications accordingly.

So, we are going to find out what how in other what are the ways, we can find out this diffusion coefficient or if it is not just diffusion coefficient, we had taken a number of phenomenological equations, where you had diffusion coefficient, thermal coefficient and viscosity coefficients. These how can they be determined, will be also taken up in subsequent lectures.

Thank you so much.