

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

Lecture – 30
Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules in Motion.

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Molecular Motion in Liquids: THE ONSAGER EQUATION

DEBYE-HÜCKEL-ONSAGER THEORY: VERIFICATION

- The test is whether the **limiting slope of a plot of experimental values of Λ_m versus \sqrt{c}** has the value as predicted by the derived equation
- A comparison of the data with the values predicted by the **Debye-Hückel-Onsager Equation** is shown for several salts in water
- The agreement is usually excellent in very dilute solutions up to about 0.02 M
- In more concentrated solutions the conductivity is usually higher than we would predict from the **Debye-Hückel-Onsager Equation**

Test of the Debye-Hückel-Onsager Equation. The lines are the limiting slopes

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If you remember in the last class, what we did was, we had talked about the Debye-Huckel-Onsager equation. We had talked about the Debye-Huckel-Onsager equation in terms of the 2 effects which generate which cause the, which is associated with the ionic atmosphere of ion, which is under the influence of electric field. The 2 effects were the electrophoretic effect and the relaxation effect. And we had we had shown that the lambda the molar conductivity of a electrolyte, then at any concentration is we can be given as lambda at any concentration lambda n will be equal to lambda m naught; that means, contribution of the limiting conditions of 0 concentration of the of the electrolyte is equal to minus a plus b into the molar conductivity infinite dilution into root over c.

So, what we had what we have derived in the equation, here we have the equation. So, if we derive that equation we can see that when the equation which we are having is the modification of the Debye Huckel equation and this is that way this was called the Debye-Huckel-Onsager theory. And now what we will look? We will look for the

verification. What we will do? We will we have taken the limiting slopes of the lambda versus under root c curves. And see whatever the values which we are getting from the equation which we have generated and what we have getting when we are doing the experiment. So, what we are trying to do? We are trying to model the equation in terms of what we usually observe for a particular type of electrolyte in a solvent system.

So, here we are having a comparison of a data, the values predicted by Debye Huckel equation in the some several salts. And the agreement which we are going to being seen, here you see, this is the conductivity versus the say concentration term, the molar conductivity plotted in the y under root c the molar concentration of the electrolyte in the x axis. See, for a various types of electrolyte system. So, if we have various type of electrolyte system, whatever we are seeing as these lines, these are the values which we are getting which we are generating from the equation of the Debye Huckel.

So, if you see the agreement of whatever we get from the theoretical values generated from the Debye-Huckel-Onsager theory or equation, and what we observe are more in parity, more in parity when the concentrations are lower. In fact, the agreement is usually very good in very dilute solutions up to say a concentration of 0.02 molar. So, and at higher concentrations, when the concentrations are much higher, which we have also discuss why the concentration is going to if increase if we increase in the concentration, the operative retarding forces are much more; so, the equations which we are developed for the Debye-Huckel-Onsager equation has a deviation. So, we see at higher concentration the observed value are different from that of the experimentally predicted.

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Molecular Motion in Liquids: THE ONSAGER EQUATION

DEBYE-HÜCKEL-ONSAGER THEORY: VERIFICATION

- According to the **Kohlrausch's law**, the **slopes of the molar conductivity (Λ_m)** curve is predicted to have:
 - $\propto \sqrt{c}$ dependence on the **molar concentration** of the electrolyte, and
 - Depend on the charge type of the electrolyte
- From the comparisons between theory and experiment we see that the **agreement is quite good** at **very low ionic strengths**, corresponding to **very low molar concentrations** (less than about 10^{-3} M, depending on the charge type).
- The straight lines in the figure represent the prediction from the **Debye-Hückel-Onsager Equation** is shown for several salts in water

Test of the **Debye-Hückel-Onsager Equation**. The lines are the limiting slopes

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So, what we can see in another diagram I am going to show the you the same thing, but in terms of the ionic strength. What Debye Huckel studied was the mobility or the coefficient of activity in terms of the ionic strength. An ionic can be obviously related to the molar concentration. So, it is going be directly proportional right. So, we are going to whatever we have predicted for the Debye Huckel theory. Let us see how it can be extrapolated when we are talking about the Debye-Huckel-Onsager equation.

According to the Kohlrausch's law, the slope of the molar conductivity; that is, Λ_m versus under root c curve is predict to have under root c dependence on the molar concentration of the electrolyte, and it also depends on the type of charge. It is not actually dependent on the actual identity of the charge involved, but it dependence on the type of charge the electrolyte has ok. It is plus 1 plus 3 plus 4: what is the type of charge it is having.

So, the according to the Kohlrausch's law, the molar conductance is going to be dependent on the under root c concentration of the electrolyte, and it is going to depend on the type of charge of the electrolyte involved. For comparison between theory and experiment, we can see that the agreement is quite good as in the previous slide also I had shown. At lower ionic strength, if you have lower ionic strength, it can be corresponding to lower molar concentration. At lower molar concentration, say 10 to the power minus 3 molar and also on the type of charge we have. You can see the strength

are actually what is predicted from the equation, and these are what we have actually in the observation when you do an experiment.

So, these lines which have the dots on them are the experimental observations, and the solid lines for the different electrolytes are given here. And we are extrapolating the line to the limiting condition of 0 ionic strength which is going to be corresponding to approaching, 0 molar strength concentration of the electrolyte. So, you see that the validity of this equation is quite good whatever we have predicted as long as the concentration of the electrolyte we are using is small. So, at limiting conditions you are at very low concentrations of the electrolyte, the equation which we have developed as Debye-Huckel-Onsager equation which is having the contribution of the ionic atmosphere taken into account; which has associated effects like electrophoretic effect and the asymmetry effect associated with it.

So, with 2 parameters taken into account we have developed and formulated the equation of the Debye-Huckel-Onsager theory. And that theory when we plotted against to compare against the experimental observations, we see that for one electrolyte you see, at lower concentration the parity is quite good, between the experimental and observation. And usually if you have a higher this is the type of depending on the type of charge you will have the different slopes of the conductivity which is associated when you are doing the measurement. And the concentration whatever you are measuring, the concentration if it is low, in the range of 0.02 to 0.01 molar concentration of the electrolyte, then we for any type of electrolyte the parity is quite good. This is the validation of the law which we so, taken time to formulate.

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Molecular Motion in Liquids: Fick's First Law of Diffusion

- We are now in a position to extend the discussion of ionic motion to cover the migration of neutral molecules **and** of ions in the absence of an applied electric field. We shall do this by expressing ion motion in a more general way than earlier, and will then discover that the same equations apply even when the charge on the particles is zero.

Fick's First Law of Diffusion

- There is an intimate connection between **the mobility of an ion in an electrical field** and the **rate at which the ion diffuses under the influence of a concentration gradient**.
- On general thermodynamic grounds, particles are expected to **spontaneously move from a region of high concentration to one of low concentration**
- The driving force for this motion of the particles is **proportional** to the negative gradient of the concentration; the **velocity of the particles are proportional to this driving force**

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Now, we move on to something different. So far we have talked about the ionic atmosphere, the ionic motion of the molecules, now we are position to extend the discussion of the ionic motion whatever we have developed to cover the migration of neutral molecules or ions in absence of a electric field. We shall do that by expressing the ion motion in general way, not like the earlier one, and then discover that the same equation which we have applied previously can be actually extended to a charge particle with of the particle of charge particle of 0 charge associated. So, that means a neutral molecule.

So, what we are trying to say that whatever we have discussed for the charge molecule under the electric field, we will try to experience the motion of the charge particle with having no charge associated with it charge on it being 0 considering as a neutral particle. And we will generalize and formulate how that can be applied system which is say having no charge associated with it. So, for that we will take a verifications and generate few laws which can associate which can which is a link between the discussions on the ionic motion of particles in a migration in electric field, to the migration of a neutral molecule in absence of a electric field.

So, one of the things which we will try to verify is the Fick's first law of diffusion. So, the in what happens in if you have the mobility of ions in electric filed? There is a connection between the mobility of ions in electric filed and at the rate at which the ions

diffuse under the electric gradient ok. So, what we have so far developed? We have developed the mobility expression, and we have develop the mobility expressions in association with a electric field. Now, we will see that we can relate conceptually the mobility of ions, instead of that we can say the diffusion of ions can take place if there is also a concentration gradient associated. On thermodynamic grounds particle is expected to spontaneously move from a higher concentration region to a lower concentration region. That means, thermodynamically any ion can be having a driving force of the to move forward or migrate depending on the concentration gradient it is associated with.

So, the driving force for the motion of these more particles will be proportional to the negative gradient of the concentration of the ions in the medium ok. So, it is the always the ions are going to diffuse from lower higher concentration region to lower concentration region. And the driving force of this movement of the migration of the ions will be proportional to the negative gradient of the concentration.

And velocity of the particles hence a supposed to be proportional to the driving force. Because whenever you are having a particles moving motion is guided by a thermodynamic force any movement which is going to be associated with that will be the speed of the molecules; hence, should be also proportional to the driving force. So, if the force or driving force is more strong the speed of the particles moving should be migrating should be more associated with it right.

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Molecular Motion in Liquids: Fick's First Law of Diffusion

Fick's First Law of Diffusion

Fick's First Law of Diffusion (that the **particle flux** is **proportional** to the **concentration gradient**) could be **deduced** from the kinetic model of gases. Let's see how it can be deduced **more generally** and that **it applies to the diffusion of species in condensed phases too.**

- Let us suppose that the **flux of diffusing particles is motion, in response to thermodynamic force, arising from a concentration gradient.**
- We have previously shown that the particles reach a **steady drift speed, s** , when the **thermodynamic force, F** , is matched by the **viscous drag.**

$$F_{\text{fric}} = f \times s \quad \text{where, } f = 6\pi a\eta \text{ (from Stokes Law)}$$

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So, let us now come in to the discussion of a flux of particle. Fick's law what does Fick's law says? Fick's law says first law Fick's law says that the particle flux is proportional to the concentration gradient. This can be deduced from the kinetic model of the gas. Let us see how it can be deduced in more general form. And it can be apply to diffusion of species in condensed phase; that means, the liquid and the solid phase as well.

So, whatever concept we are develop from the kinetic model, we are going to be is using the same concept to deduce use it as a generalized concept to deduce the diffusion of species in a non electric under no non electric field, no electric field associated, and also in for the species which is actually not charged, or it is move movement of the particles in the solid or liquid phase. So, let us suppose what we have so far, the flux of diffusion of diffusing particle in motion in response of a thermodynamic force arises from a concentration gradient.

So, let us assume this is the first assumption we are going to think of; that the flux of the diffusing particle in which is motion is in response to the thermodynamic force arising because of concentration gradient. This is known to us we have known that this is the phenological logical equations which we have already had. So, we are going to assume that, now next one what we have already done? We have previously shown that the particles move with a terminal speed when the thermodynamic force matches with that of the viscous drag associated with the field.

So, if that if you remember, the thermodynamic forces is going to be matched with the viscous drag, and then speed associated with that is going to be known as the drift speed. So, the particles move with the steady terminal speed or drift speed, when you have the thermodynamic force balancing the viscous drag. So, this was the concept we had used when in a application of electric field, but we are not talking about the electric field, here we are talking only about the particles moving in a viscous medium.

And if they are if they are supposed to be moving, then it is essential to have if they are having moving with a steady drift speed or a constant speed. And this speed is known as the drift speed or terminal speed. This speed should be can be achieved by the particle only when the thermodynamic forces apply operative on the particle is matched by the viscous drag associated in the medium.

So, this is the expression we have. So, we have the frictional force which is thermodynamic force is going to be proportional to the speed of the particles. So, this is what we can write.

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Molecular Motion in Liquids: Fick's First Law of Diffusion

- We can therefore say that this **drift speed, s** , is **proportional to the thermodynamic force, F**
So, we can say: $s \propto F$
- We have also shown that the **particle flux, J** , is **proportional to the drift speed, s**
Flux of particles is the number of particles, moving with speed, s , in x direction, time interval, Δt , passing through the window of area, A , divided by the area of the window and the duration of the interval)
 $J(\text{flux of particles}) = \frac{s\Delta tAcN_A}{A\Delta t} = scN_A$
 Therefore, we can say: $J \propto s$
- Again from the **phenomenological equations** we know that the **driving force for the motion of particles, F** , is **proportional to the negative gradient of the concentration, dc/dx**
 Therefore, we can say: $F \propto -\frac{dc}{dx}$

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So, we can write the drift speed is proportional to the thermodynamic force, because if the thermodynamic force is balanced by the viscous force, only then you will get the achieve the drift speed for the particle which is associated. So, s is going to be proportional to the F the thermodynamic force which is operative on the particle. And this is the speed with which the molecules or ions or whatever we are looking into particles and moving with a at a steady rate.

Now, again we have a relation where the flux of particle is proportional to the speed of the particle. If you remember, we had talked about the flux of a particle, how it was defined. Suppose we have a number of particles associated with a system b having a concentration c moles per litre. So, if you want to find out the number density we had taken, it is going to be concentration into the number of Avogadro number, will give you the number of particles associated with it. So, the flux of particles which is moving with a speed s in the say in x direction in the time interval Δt passing through a window of area A will be divided by the area of the window and the duration of the interval Δt , is going to give you the flux of the particle.

So, $s \Delta t$ into A is the volume element which is containing the total number of this is the volume element, area into this is was the distance speed into time was giving in the distance. So, this was the volume element in which with the particle the total number of particles in the volume element of this was considered, that into the concentration of in moles per litre into the Avogadro number gives you the total mole number of concentration of the particles; that divided by the area into the time Δt gives you the flux of particle.

So, if you see this these are going to be cancelled outs. This we have already derived previously for gas system when we are talking about molecules moving in the gaseous medium. We have done that, we have also seen how this equation gets modified by a new values here, when we are having a electric field associated. So, for we have taken we have also derived the flux of ions, but we let us on the concentrate of on the flux of particles. So, flux of particles as you see will be proportional to the speed of the molecules associated in the system.

So, we have what we have generated? We have generated another relationship of dependence; where the flux of particles represented by J will be proportional to the speed of the particle. So, this is the drift speed which we are talking about. So, so J is proportional to s , right? Now, again we go back to the phenomenological equation which we had. The driving force of the molecules of a particle F will be proportional to the negative gradient of the concentration. So, if c is the molar concentration associated for a particular system, and if the particles are moving say in the particular x direction, then the driving force which is going to drive the molecules to or particles to move along the medium, the migration of the particles will be proportional to what will be proportional to the gradient and concentration, negative gradient and concentration.

So, negative gradient and concentration is actually given by minus dc by dx ; that means, we are talking about the movement of the particle in the x direction. How the concentration of the particles are changing when the particles are moving in the x direction? And in this x direction what we are looking into? What is the driving force the for the particles to move along the x direction, it is the concentration, it is the driving force is the concentration of the difference in concentration along the x axis. So, the particles are going to move from a higher concentration to a lower concentration.

So, the driving force is proportional to the gradient negative gradient in the concentration. So, what we have? We have generated we have generated 3 chain of proportionalities.

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Molecular Motion in Liquids: Fick's First Law of Diffusion

- From the chain of proportionalities: $s \propto F$ $J \propto s$ $F \propto -\frac{dc}{dx}$

We can deduce: J (particle flux) $\propto -\left(\frac{dc}{dx}\right)$

And this is the content of the **Fick's First Law of Diffusion**

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The drift speed being proportional to the driving force; which we have from the drift speed being attend only when the viscous drag and the thermodynamic forces of balance. So, it is going the speed which is associated will be proportional to the thermodynamic force which is operative. Then we have seen the flux of particle; which is moving in a medium should be proportional to the speed with which the particles are moving the terminal speed. And we have seen that the thermodynamic force which is operative for a migration of particle along the medium will be depending on the negative gradient of the concentration.

So, if you see here s is proportional to F , J is proportional to s . So, what we can say? We can say that s is proportional to F , and F proportional to J , and J is proportional to; can be taken as proportional to the change in concentration. So, what we have? We have derived the expression which is the flux of particle J will be proportional to the concentration gradient along the medium, ok. So, what we have in the form? We have generated the contents of the first law of diffusion. So, the first law of diffusion says that the flux of particle will be proportional to the negative gradient of concentration when the particles

are moving along the x axis. So, the chain of proportionalities which we have generated; see these equations we are not saying is it is not over this lecture that we have developed.

We have developed the speed of the particles being proportional to f when we were discussing when the particles under moving under electric field, that time we say that the electric field will be balanced by the this thermodynamic force which is acting. But eventually what it what essentially means that wherever particle is moving with a steady speed, steady or constant speed it has to have a condition where that viscous force and a thermodynamic forces are going to balance.

So, that concept was already there we have extended that. Now we also considered when we are talking about a particle, it need not be charged. A we say that it let it be a say from kinetic theory whatever we have derive, any particle moving in a particular medium. So, if they are particles are moving with a particular speed. Then the flux of that particle what found to be proportional to the speed of the particles in the system.

And again from the thermodynamic expression of thermodynamic force; which is supposed to be proportional to the gradient in the number of ions or number of molecules of particles in a system. These 3 proportionalities if we combine if we take the analogist, then we come done to the fact that the flux of particle will be proportional to the negative gradient of concentration.

So, I think we will discuss till this for today. We will talk about the other equations in the later class.