Transport Phenomena in Biological Systems

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Lecture - 57

Simultaneous Concentration Gradient and Electrical Potential Gradient

Welcome, in today's class, let us continue looking at multiple driving forces resulting in a flux of a certain kind. This is the first example that we are going to look at in some detail and this has significant applications or it has great significance for the human body otherwise and so on so forth. As you will see, when we go through today's class, this is on simultaneous concentration gradient and electrical potential gradient and we are going to look on the effect of these 2 simultaneous gradients on mass transport.

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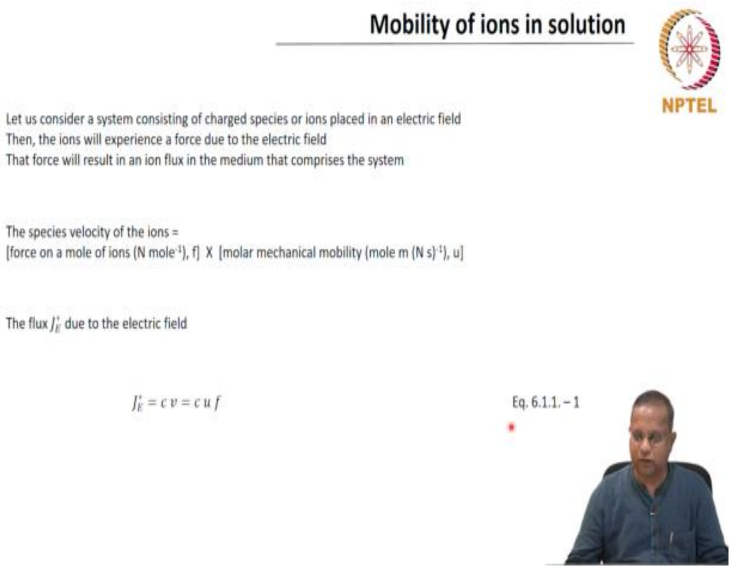

Mobility of ions in solution

Let us consider a system consisting of charged species or ions placed in an electric field
Then, the ions will experience a force due to the electric field
That force will result in an ion flux in the medium that comprises the system

The species velocity of the ions =
[force on a mole of ions (N mole^{-1}), f] X [molar mechanical mobility (mole m (N s)$^{-1}$), u]

The flux J_E^+ due to the electric field

$$J_E^+ = c\,v = c\,u\,f \qquad \text{Eq. 6.1.1.}-1$$

Let us first understand or we need to understand the principles that govern the mobility of ions in solution or the way we understand it, to provide us with some strong base, we need to be clear about it. Some of this you may have seen as final equations in your previous courses, classes and so on and so forth. Here we would look at it from our point of view we will try to understand it from our requirements and so on.

Let us consider a system consisting of charged species or ions and we are going to place that in an electric field that is the situation here. Then, the ions will experience a force due to the electric field. We have already seen in the previous one of the previous chapters, electric charge flux, how this could happen? The disruption of the cloud and so on so forth can go back and verify that.

So, these ions will experience a force due to the electric field that is placed over this setup or system let us say, that force will result in an ion flux in the medium that comprises the system. So, there is a certain medium in the system and these ions are in the medium and the electrical force or electric field that is applied will result in an ion flux or could result in an ion flux in the medium.

In such a situation, the species velocity of ions recall our mass flux, how we talked of the velocity of a certain species $\rho_i v_i$ recall that. Here, we were talking of species velocity of ions, which are charged particles with charged molecules whatever, we are going to write the species velocity of ions as a product of the force on a mole of ions, that is Newton per mole(N/mol), which is represented by a certain f times something called a molar mechanical mobility.

This is a new term molar mechanical mobility, the developments have taken place on the basis of this term and therefore, we are going to also develop our things on the basis of this stuff. So, the units of molar mechanical mobility are quite complex as you can see, I get back things out then you could find that molar mechanical mobility has the units of mole meter per Newton second, and is usually represented by this symbol u.

We are going to use the symbol u for the molar mechanical mobility in this course, and the symbol f, lowercase f, for the force on a mole of ions. The flux due to the electric field, the molar flux due to the electric field, which we are going to represent as J^*_E in 1 direction, we do not worry about the vector, but it is actually a vectorial quantity. So the flux due to the electric field, J^*_E is nothing but the product of concentration into velocity we have already seen this.

This velocity the species velocity is written as a product of the molar mechanical mobility and the force on a mole of ions.

$$J_E^* = c\,v = c\,u\,f \qquad (6.1.1\text{-}1)$$

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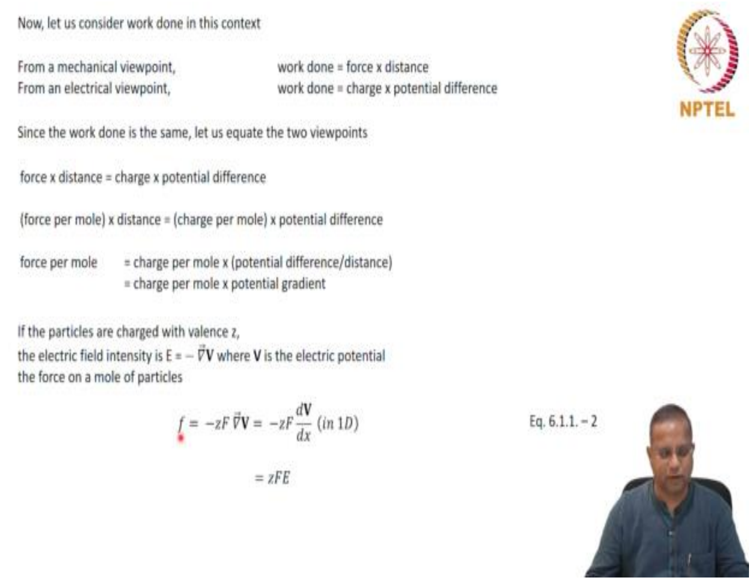

Now, let us consider work done in this context

From a mechanical viewpoint, work done = force x distance
From an electrical viewpoint, work done = charge x potential difference

Since the work done is the same, let us equate the two viewpoints

force x distance = charge x potential difference

(force per mole) x distance = (charge per mole) x potential difference

force per mole = charge per mole x (potential difference/distance)
= charge per mole x potential gradient

If the particles are charged with valence z,
the electric field intensity is $E = -\vec{\nabla}\mathbf{V}$ where **V** is the electric potential
the force on a mole of particles

$$f = -zF\,\vec{\nabla}\mathbf{V} = -zF\frac{d\mathbf{V}}{dx}\ (in\ 1D) \qquad \text{Eq. 6.1.1.} - 2$$

$$= zFE$$

Now, we are going to consider the work done in this context. Let us try to understand the various ways of looking at work. You may be familiar with some of these you may not be so comfortable with some of these. It is good to make sure that we understand this clearly. From a usual mechanics mechanical viewpoint, physics viewpoint, work done is force times distance, or classical physics viewpoint work done is force per distance, force times distance.

From an electrical viewpoint, work done is charge times potential difference. We all know this from our highest secondary school high school. The work done in an electrical system is the charge times the potential difference the work done is the same, it is just a view that is different either you look at it from a mechanical point of view or an electrical point of view. Since the work done is the same, you are going to equate the 2 viewpoints here because this is a system which charges and electrical aspect.

So force times distance equals charge times potential difference, where equating these 2 right hand sides here, to get force times distance equals charge times the potential difference. So force if we divide by both sides by mole and take that along with this force per mole times distance equals charge per mole times the potential difference. Therefore, the force per mole that we have been talking about is nothing but charge per mole times the potential difference divided by the distance here and what is this nothing but the potential gradient.

So force per mole is charge per mole times the potential gradient here. Now if the particles are charged with a valance z it has a valency of z and the electric field intensity is given as -∇V where V is the electric potential as we have already seen. The force on a mole of particles, force per mole force on a mole of particles, which we said we will represent by the lowercase f is nothing but minus zFV.

So, if you want to write this in 1 dimension, you could write this as -zF(dV/dx), if it is a 1 dimensional case, we could write it this way, and this is a 3 dimensional case. In a 3 dimensional case, you write it this way. Let us number this as 6.1.1 - 2 and this is nothing but E the electric field intensity. Therefore the force per unit mole or force per mole force on a mole of particles is nothing but zFE which is represented by the lowercase f.

If the particles are charged with valence z, and the electric field intensity is $E = -\vec{\nabla}\mathbf{V}$ where $\mathbf{V}$ is the electric potential, the force on a mole of particles is given by

$$f = -zF\,\vec{\nabla}\mathbf{V} = -zF\,\frac{d\mathbf{V}}{dx}\,(\text{in 1D}) \qquad (6.1.1\text{-}2)$$
$$= zFE$$

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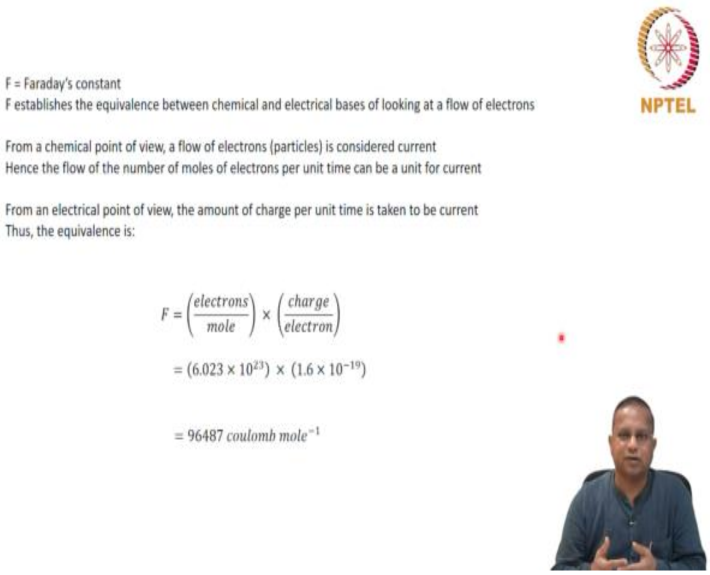

F = Faraday's constant
F establishes the equivalence between chemical and electrical bases of looking at a flow of electrons

From a chemical point of view, a flow of electrons (particles) is considered current
Hence the flow of the number of moles of electrons per unit time can be a unit for current

From an electrical point of view, the amount of charge per unit time is taken to be current
Thus, the equivalence is:

$$F = \left(\frac{electrons}{mole}\right) \times \left(\frac{charge}{electron}\right)$$
$$= (6.023 \times 10^{23}) \times (1.6 \times 10^{-19})$$
$$= 96487\ coulomb\ mole^{-1}$$

F happens it is called the Faraday's constant, as you all know, where it comes about. It is the constant of proportionality between zE and F, the force and a mole you divided by the valency times the electric field intensity. That is the Faraday's constant, this is significance just make a note of this. So F establishes the equivalence between chemical and electrical basis of looking at a flow of electrons.

Let us say because the flow of electrons is typically considered current in the classic electrical concept and of course, we could also have a chemical view on things mole and so on so forth we have gotten. So, both of those things go together here, F essentially establishes the equivalence between the chemical and electrical basis of looking at the flow of electrons that is it.

We will strengthen that as we go along from a chemical point of view, a flow of electrons is considered current you all know this. Hence, the flow of the number of moles of electrons per unit time can be unit of current or the unit for current. From an electrical point of view, the amount of charge per time is taken to be current, we know this; we have defined it this way I thus the equivalence is electrons per mole times charge per electron.

$$F = \left(\frac{\text{Electrons}}{\text{Mole}}\right) \times \left(\frac{\text{Charge}}{\text{Electron}}\right) = (6.023 \times 10^{23}) \times (1.6 \times 10^{-19})$$
$$= 96487 \text{ coulomb mole}^{-1}$$

And this is the basis for the Faraday’s constant it essentially establishes the equivalence between the chemical and electrical basis of looking at a flow of electrons or looking at current. Here, we are looking at the movement of ions, movement of charged particles, and therefore we need to understand this.

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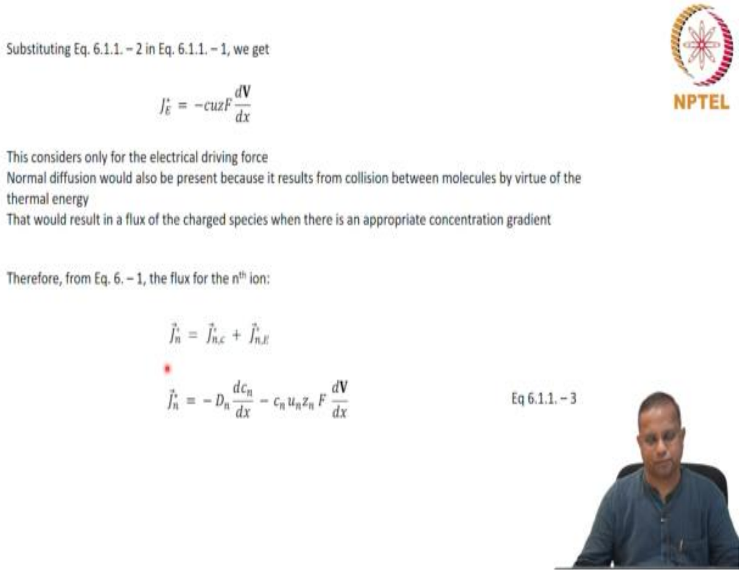

Substituting Eq. 6.1.1. – 2 in Eq. 6.1.1. – 1, we get

$$J_E^* = -cuzF\frac{d\mathbf{V}}{dx}$$

This considers only for the electrical driving force
Normal diffusion would also be present because it results from collision between molecules by virtue of the thermal energy
That would result in a flux of the charged species when there is an appropriate concentration gradient

Therefore, from Eq. 6. – 1, the flux for the nth ion:

$$\vec{J}_n^* = \vec{J}_{n,c}^* + \vec{J}_{n,E}^*$$

$$\vec{J}_n^* = -D_n\frac{dc_n}{dx} - c_n u_n z_n F\frac{d\mathbf{V}}{dx} \qquad \text{Eq 6.1.1.} - 3$$

From Eq. 6.1.1-1, in 1D

$$J_E^* = -cuzF\frac{d\mathbf{V}}{dx}$$

So, we are going to substitute for f using zFE and if we do that we get J^*_E due to the electric field this E represents electric field is nothing but cuzF(dV/dx) you have substituted for the force per mole in terms of u and c and so on so forth and therefore, we have this.

So, this considers only the electrical driving force, normal diffusion is always present, as long as there is a concentration gradient diffusion mass diffusion will be present this you cannot avoid that at all, as long as there is a driving force. So, normal diffusion would also be present because it results from collision between molecules by virtue of thermal energy. And as long as you do not reach absolute 0, this is definitely going to happen.

That would result in a flux of charged particles when there is an appropriate concentration gradient. So, since you have a concentration gradient or if you have a concentration gradient in these systems, in addition to the electric field that is imposed then you have motion due to both an electrical driving force as well as the concentration gradient driving force. So, that is the situation here.

So, the flux of for the n^{th} ion remember our equation 6 - 1, it said that a flux is the sum of the vectorial sum of fluxes from the different driving forces we talked about concentration gradient electrical c E, and then P pressure gradient and T a temperature gradient and so on so forth. So, from that equation for the flux for the n^{th} ion can be written as J^*_n the molar flux here.

Therefore, a star J^*_n a vector is nothing but the sum of vectorial sum of the $J^*_{n,C}$ due to the concentration gradient plus $J^*_{n,E}$ due to the electrical potential gradient, or an electric field that is set electric field intensity is nothing but the potential gradient we know that, therefore, let us substitute the terms we know that the concentration gradient flux is given by Fick's first law.

$$\begin{aligned}\vec{J}^*_n &= \vec{J}^*_{n,c} + \vec{J}^*_{n,E} \\ &= -D_n \frac{dc_n}{dx} - c_n u_n z_n F \frac{d\mathbf{V}}{dx} \qquad (6.1.1\text{-}3)\end{aligned}$$

. So, this expression which is equation 6.1.1 - 3 gives us the combined effect of a concentration gradient and an electrical potential gradient on the mass flux of the n^{th} ion the molar flux of the n^{th} ion.

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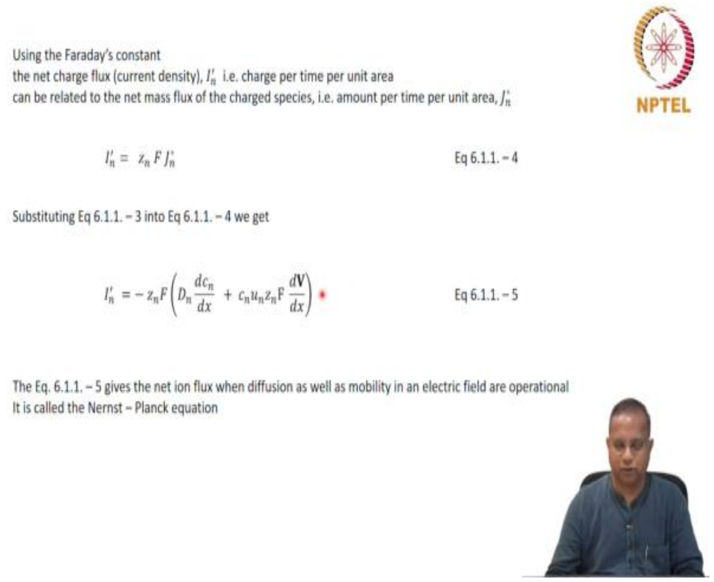

Using the Faraday's constant
the net charge flux (current density), I'_n i.e. charge per time per unit area
can be related to the net mass flux of the charged species, i.e. amount per time per unit area, J^*_n

$$I'_n = z_n F J^*_n \qquad \text{Eq 6.1.1. – 4}$$

Substituting Eq 6.1.1. – 3 into Eq 6.1.1. – 4 we get

$$I'_n = - z_n F \left(D_n \frac{dc_n}{dx} + c_n u_n z_n F \frac{d\mathbf{V}}{dx} \right) \qquad \text{Eq 6.1.1. – 5}$$

The Eq. 6.1.1. – 5 gives the net ion flux when diffusion as well as mobility in an electric field are operational
It is called the Nernst – Planck equation

Now using the Faraday's constant, the net charge flux lots of other current density we do not use system the charge flux I_n’, which is the charge per time per unit area regular flux rate we are now comfortable with it can be related to the net mass flux of the charged species that is amount per time per unit area, net mass flux of the charged species, $z_n FJ^*_n$.

So, this is the charge per time per unit area. So, we have used the Faraday's constant and converted this flux the molar flux into the current. That is essentially what Faraday's constant uses us also converts the movement to electrical terms in this case, here we use to represent it as the charge per time per unit area equation 6.1.1 - 4. Now if you substitute 6.1.1 - 3 into 6.1.1 - 4 what is 6.1.1 - 3? It was this where you have a combined expression for the molar flux of n.

$$I'_n = z_n F J^*_n \qquad (6.1.1\text{-}4)$$

Substituting Eq. 6.1.1-3 into Eq. 6.1.1-4 gives

$$I'_n = - z_n F \left(D_n \frac{dc_n}{dx} + c_n u_n z_n F \frac{d\mathbf{V}}{dx} \right) \qquad (6.1.1\text{-}5)$$

The above equation that gives the net ion flux when diffusion as well as mobility in an electric field are operational, is called the Nernst-Planck equation.

So, the net ion flux when diffusion as well as mobility in an electric field are operational and this equation which gives us the net ion flux under these conditions, when diffusion and mobility in an electric field are operation is called the Nernst Planck equation. So, you may not very sure that you come across this you will have come across some other equation which we see later. This is called the Nernst Planck equation.

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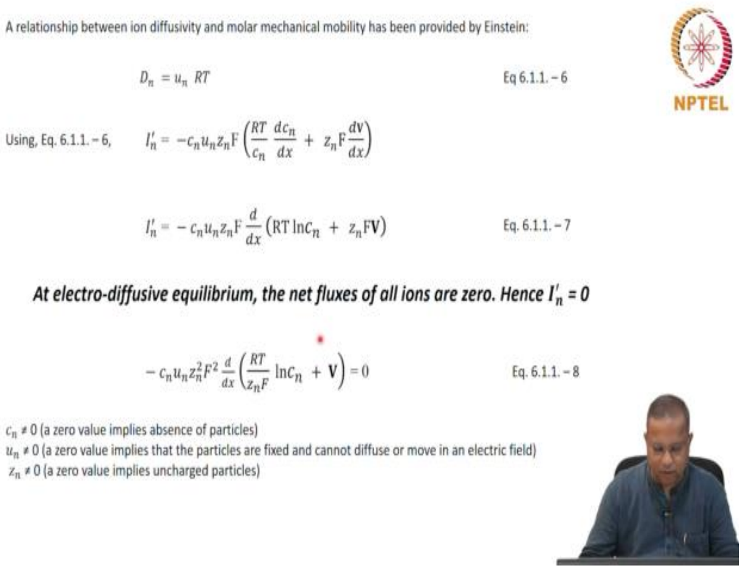


A relationship between ion diffusivity and molar mechanical mobility has been provided by Einstein:

$$D_n = u_n RT \qquad \text{Eq 6.1.1.} - 6$$

Using, Eq. 6.1.1. – 6, $I'_n = -c_n u_n z_n \mathrm{F}\left(\frac{RT}{c_n}\frac{dc_n}{dx} + z_n \mathrm{F}\frac{d\mathrm{V}}{dx}\right)$

$$I'_n = -c_n u_n z_n \mathrm{F}\frac{d}{dx}(\mathrm{RT}\ln c_n + z_n \mathrm{F}\mathbf{V}) \qquad \text{Eq. 6.1.1.} - 7$$

At electro-diffusive equilibrium, the net fluxes of all ions are zero. Hence $I'_n = 0$

$$-c_n u_n z_n^2 F^2 \frac{d}{dx}\left(\frac{RT}{z_n F}\ln c_n + \mathbf{V}\right) = 0 \qquad \text{Eq. 6.1.1.} - 8$$

$c_n \neq 0$ (a zero value implies absence of particles)
$u_n \neq 0$ (a zero value implies that the particles are fixed and cannot diffuse or move in an electric field)
$z_n \neq 0$ (a zero value implies uncharged particles)

The relationship between ion diffusivity D or D_n in this case, and molar mechanical mobility has been provided by Einstein, he did a lot of work on these aspects, he has provided us with a relationship between ion diffusivity and molar mechanical mobility, which we will directly use here, we are not going to get into how that arises and so on and so forth. If you are interested, you can go back into archives, and take a look at those original papers to see.

But here we are just going to use the relationship between ion diffusivity and molar mechanical mobility that is provided by Einstein or Einstein's relationship. Einstein's relationship is rather simple, simple looking D_n which is the diffusivity is nothing but the molar mechanical mobility. See, this thing comes in this foundation that is the reason why we have been developing things in the form in terms of the molar mechanical mobility. So diffusivity equals a molar mechanical mobility times RT, there is a relationship Einstein's relationship therefore let us number this 6.1.1 - 6

$$D_n = u_n RT \qquad (6.1.1\text{-}6)$$

Therefore

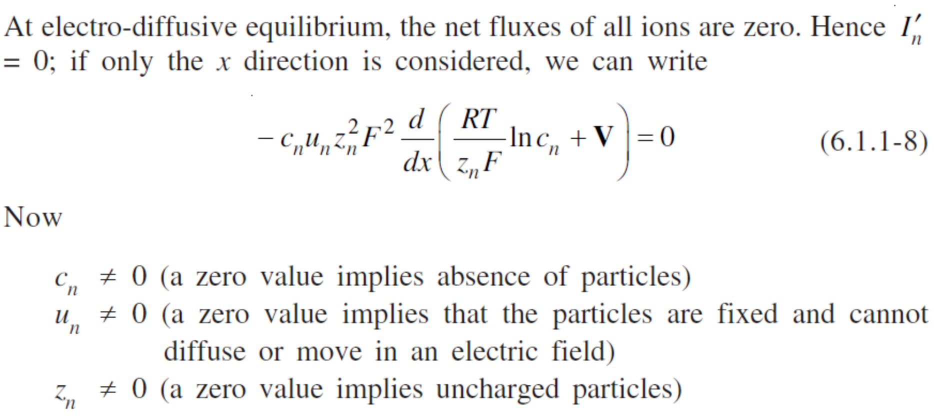
$$I'_n = -c_n u_n z_n F\left(\frac{RT}{c_n}\frac{dc_n}{dx} + z_n F\frac{d\mathbf{V}}{dx}\right)$$

or

$$I'_n = -c_n u_n z_n F\frac{d}{dx}(RT\ln c_n + z_n F\mathbf{V}) \qquad (6.1.1\text{-}7)$$

That moment in one direction equals a moment in the other direction. It is a dynamic equilibrium always, therefore, there is a moment in one direction there is a moment in the other direction. We do not deny that at all, only thing is that the rates are matched. That is what equilibrium is. The net fluxes of all ions are 0. That is the concept of electro diffusive equilibrium.

Therefore this net ion flux I_n’ has to be equal to 0. So note this, so this is the way we are going to represent the electro diffusive equilibrium, I_n’= 0. So if you substitute I_n’= 0, you could directly write this, we are going to pull out common more common terms, c_n u_n, we are going to pull out another z_n, therefore we need to divide this by z_n this, this becomes z_n^2, you are going to pull out F also.



At electro-diffusive equilibrium, the net fluxes of all ions are zero. Hence I'_n = 0; if only the x direction is considered, we can write

$$-c_n u_n z_n^2 F^2 \frac{d}{dx}\left(\frac{RT}{z_n F}\ln c_n + \mathbf{V}\right) = 0 \qquad (6.1.1\text{-}8)$$

Now

$c_n \neq 0$ (a zero value implies absence of particles)
$u_n \neq 0$ (a zero value implies that the particles are fixed and cannot diffuse or move in an electric field)
$z_n \neq 0$ (a zero value implies uncharged particles)

F is a Faraday's constant, certainly not 0.So this term cannot be 0 which means this has to be equal to 0 electro diffusive equilibrium this term alone can be 0.

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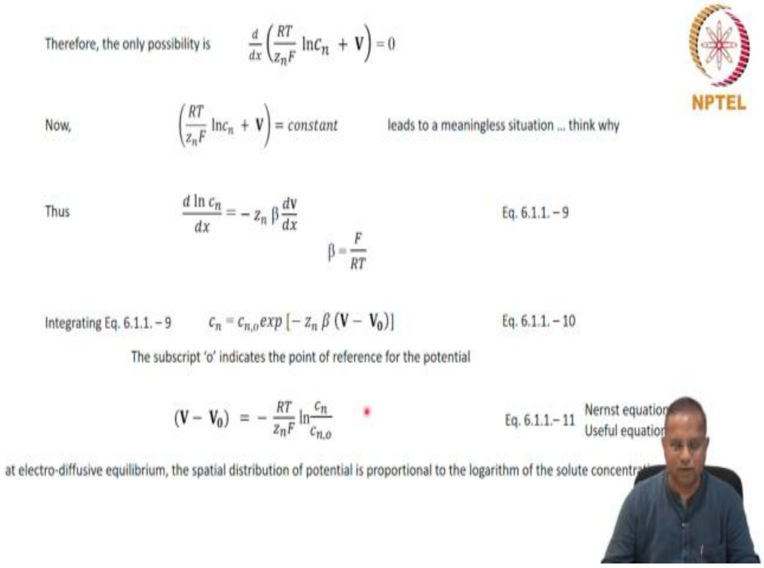

Therefore, the only possibility is $\frac{d}{dx}\left(\frac{RT}{z_n F}\ln c_n + \mathbf{V}\right) = 0$

Now, $\left(\frac{RT}{z_n F}\ln c_n + \mathbf{V}\right) = constant$ leads to a meaningless situation ... think why

Thus $\frac{d\ln c_n}{dx} = -z_n \beta \frac{d\mathbf{V}}{dx}$ Eq. 6.1.1. – 9

$\beta = \frac{F}{RT}$

Integrating Eq. 6.1.1. – 9 $c_n = c_{n,o} exp\left[-z_n \beta \left(\mathbf{V} - \mathbf{V_0}\right)\right]$ Eq. 6.1.1. – 10

The subscript ‘o’ indicates the point of reference for the potential

$(\mathbf{V} - \mathbf{V_0}) = -\frac{RT}{z_n F}\ln\frac{c_n}{c_{n,o}}$ Eq. 6.1.1.– 11 Nernst equatio
Useful equatio

at electro-diffusive equilibrium, the spatial distribution of potential is proportional to the logarithm of the solute concentr

Now let us examine this further, this is equal to 0. Now this is a derivative. So we all know that the derivative of a constant equals 0. So, this could be a constant, do not be so confident. This could be a constant, maybe not, we will see. If this is a constant, what does it mean? It means a meaningless situation. What I want you to do is pause the video here and go term by term and figure out why this cannot be 0 or the argument of this derivative cannot be 0, I mean cannot be a constant, not a 0 cannot be a constant.

So think about why this cannot be a constant. Take a few minutes, pause the video, think about it twice. I would let you figure out why this cannot be a constant. If this is a constant, it leads to a meaningless situation, think about it. If you cannot get to the answer, raise a question in the forum we will discuss these things. Therefore, the only way by which this term would be 0 is that the argument itself is 0.

Thus

$$\frac{d}{dx}\left(\frac{RT}{z_n F}\ln c_n + \mathbf{V}\right) = 0$$

The whole derivative being zero implies that the terms inside the bracket need to be a constant – a physically irrelevant situation with both c_n and $\mathbf{V}$ being constants. Therefore, let us see the situation as

$$\frac{d\ln c_n}{dx} = -z_n \beta \frac{d\mathbf{V}}{dx} \qquad (6.1.1\text{-}9)$$

where

$$\beta = \frac{F}{RT}$$

Equation 6.1.1-9 can be integrated to give

$$c_n = c_{n,o} \exp\left[-z_n \beta (\mathbf{V} - \mathbf{V}_0)\right] \qquad (6.1.1\text{-}10)$$

The subscript ‘o’ indicates the point of reference for the potential.
Thus

$$(\mathbf{V} - \mathbf{V}_0) = -\frac{RT}{z_n F}\ln\frac{c_n}{c_{n,o}} \qquad (6.1.1\text{-}11)$$

i.e. at electro-diffusive equilibrium, the spatial distribution of potential is proportional to the logarithm of the solute concentration. Equation 6.1.1-11 is very useful, and is referred to as the Nernst equation.

This is the Nernst equation. I am sure you would have heard the term you would have seen the equation. I am sure you recognize this equation, Nernst equation and very useful equation. We are going to use it again and again. At electro diffusive equilibrium, the spatial distribution at electric diffusive equilibrium, spatial distribution of potential is proportional to the logarithm of this and solute concentration.

You know that the negative the ln A - ln B is ln(A / B). Therefore there is actually ln A - ln B. So at electro diffusive equilibrium I’ equals constant, the spatial distribution of potential is proportional to the logarithm of the solute concentration. This is essentially the meaning of Nernst equation. I think we need to stop here. We have been at this for some time now. I think it is best to stop here. New information therefore I will let you process it. And let us continue in the next class. See you.