Colloids and Surfaces
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Lecture – 31
Potential Distribution Near Planar Surfaces: Derivation of the Poisson - Boltzmann Equation

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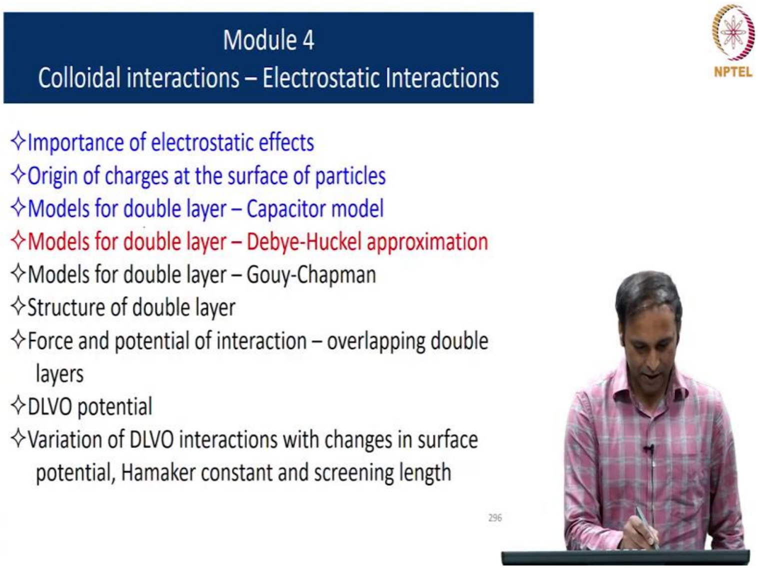

Module 4
Colloidal interactions – Electrostatic Interactions

- ✧Importance of electrostatic effects
- ✧Origin of charges at the surface of particles
- ✧Models for double layer – Capacitor model
- ✧Models for double layer – Debye-Huckel approximation
- ✧Models for double layer – Gouy-Chapman
- ✧Structure of double layer
- ✧Force and potential of interaction – overlapping double layers
- ✧DLVO potential
- ✧Variation of DLVO interactions with changes in surface potential, Hamaker constant and screening length

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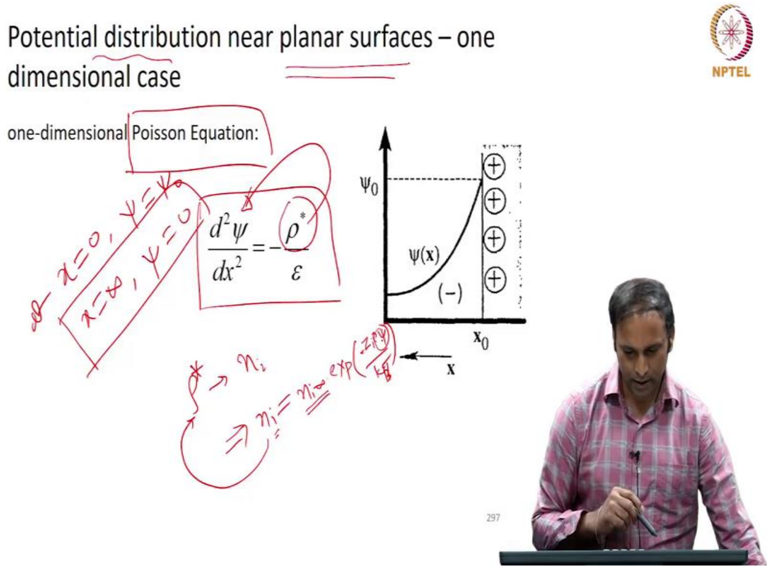

Potential distribution near planar surfaces – one dimensional case

one-dimensional Poisson Equation:

$$\frac{d^2\psi}{dx^2} = -\frac{\rho^*}{\varepsilon}$$

at $x = 0, \psi = \psi_0$

$x = \infty, \psi = 0$

$\rho^* \rightarrow n_i$

$\Rightarrow n_i = n_{i\infty} \exp\left(\frac{-z_i e\psi}{kT}\right)$

So, we will continue with the models for electrical double layers. So, what we were trying to do in the previous lecture was looking at potential distribution near a planar surface. We took a 1 dimensional case that means we are trying to solve 1 dimensional Poisson equation and this is what the expression is, and we would like to solve this at the boundary conditions that at x = 0 potential at the surface itself.

And x is equal to infinity, the potential is going to be 0. The potential would be 0 to infinity because either the concentration of ions at infinity is 0 or it is such that the concentration of positive ions and negative ions is equal such that the overall potential gets canceled. That is the reason why at x is equal to infinity, psi going to be 0. And we said that if you really want to solve this, I would somehow want to express rho star in terms of psi.

So, the way to do this would be, we know that the rho star which is the charge density, the charge density would be related to again the concentration of ions that you have the solution. And we had said that this n i is related to n i infinity that is the concentration of i th type of ions in solution. It depends on what is the concentration of the same species at infinity multiplied by a factor, which is exponent of – z i e times psi divided by $k_B T$. That is what we mentioned. And if I know n i star, I can get rho star because you know, n i is related to psi therefore, I am able to express rho star in terms of psi that is what we are trying to do.

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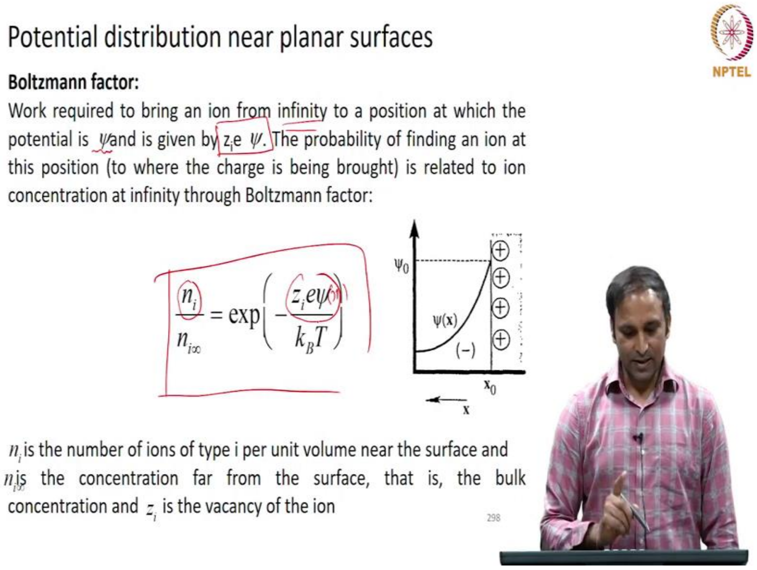

Potential distribution near planar surfaces

Boltzmann factor:

Work required to bring an ion from infinity to a position at which the potential is ψ and is given by $z_i e\ \psi$. The probability of finding an ion at this position (to where the charge is being brought) is related to ion concentration at infinity through Boltzmann factor:

$$\frac{n_i}{n_{i\infty}} = \exp\left(-\frac{z_i e \psi(x)}{k_B T}\right)$$

n_i is the number of ions of type i per unit volume near the surface and $n_{i\infty}$ is the concentration far from the surface, that is, the bulk concentration and z_i is the vacancy of the ion

So, in this Boltzmann factor, this quantity z i e psi tells you something about what is the work that has to be done to bring any specific ion. In this case, we are considering n i to bring it from infinity to a position where the potential is psi.

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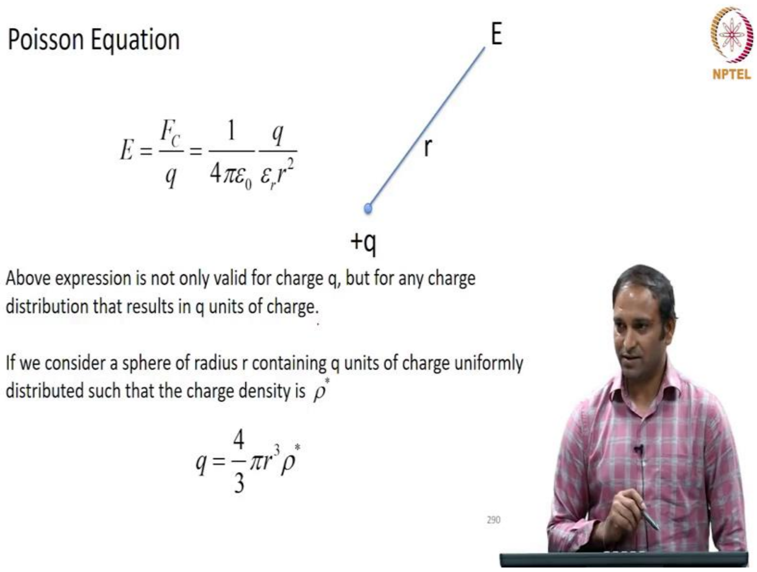

Poisson Equation

$$E = \frac{F_C}{q} = \frac{1}{4\pi\varepsilon_0}\frac{q}{\varepsilon_r r^2}$$

Above expression is not only valid for charge q, but for any charge distribution that results in q units of charge.

If we consider a sphere of radius r containing q units of charge uniformly distributed such that the charge density is ρ^*

$$q = \frac{4}{3}\pi r^3 \rho^*$$

And that work that has to be done is given by z i times e times psi. rho star is also a function of x. So, when I said this psi is actually also a function of x. We defined rho star. Let us go back. The way the rho star was defined here. We defined it as a charge density. So, basically it depends on the distribution of ions in the solution.

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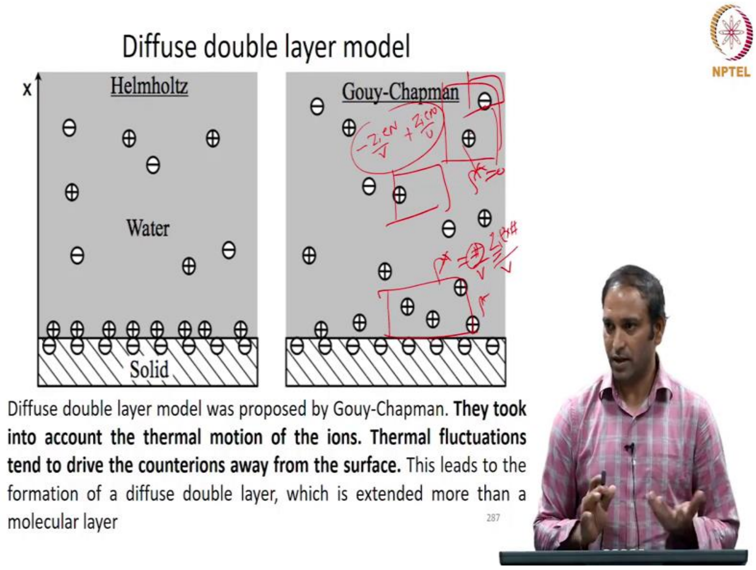

Diffuse double layer model

Diffuse double layer model was proposed by Gouy-Chapman. **They took into account the thermal motion of the ions. Thermal fluctuations tend to drive the counterions away from the surface.** This leads to the formation of a diffuse double layer, which is extended more than a molecular layer

If you look at a charge surface, we know that the concentration of counter ions in solution, if you look at the concentration, let us go back to this model, If we look at this model, let us take you know, finite volume here and finite volume somewhere there and find out what the distance, very far away distance. Now, if you look at, you know, the fact that you know, the, the concentration of counter ions is going to be higher here.

And, if you go to account for the polarity, everything. There will be some, you know, rho star that you can calculate, which basically is the number of ions that you have per unit volume that I am taking. If I take a finite volume. However, if I go to a very far, if I look at, you know, I mean let us say, I am taking a similar volume here. The fact that you know, I have, you know, both positive and negative and if there an equal number your rho star is going to be 0.

Because you know, there is a contribution that comes from the positive ion and there is also a contribution that comes from negative ion, so if you can say that overall charge density, even though it is number. I mean, this is the total charge per unit volume. The total this is not the number. It is not the number density it is the charge density that means if I have ion whose valence is i multiplied by e, multiplied by the total is a number as well.

The total charge divided by the unit volume. So, if I go to a very far away distance, the fact that you know you will have a equal probability of finding both positive and negative ions, so I am going to have charge density which could be – z i times e divided by volume times the number. For example and + z i times e multiply by number by volume. Therefore, that becomes essentially 0. So, this is actually rho star is actually spatially varying when you think about, the total charge in the whole system is going to be electrically neutral.

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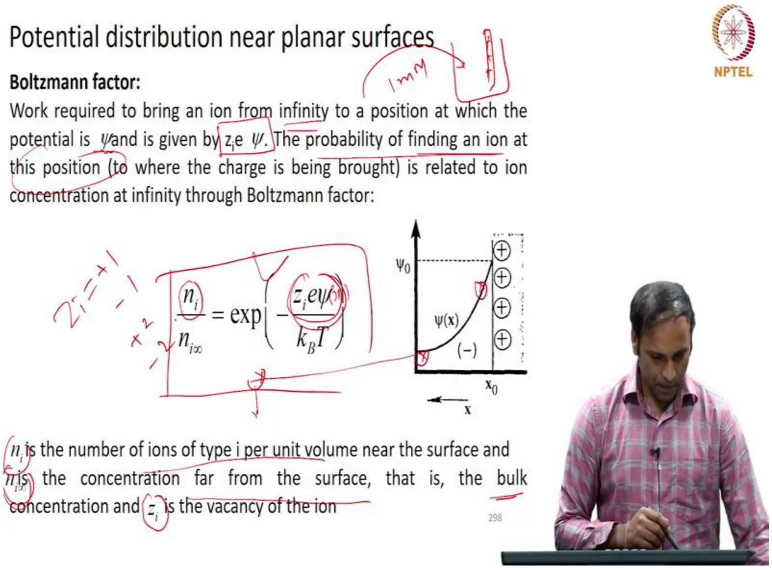

Potential distribution near planar surfaces

Boltzmann factor:

Work required to bring an ion from infinity to a position at which the potential is ψ and is given by $z_i e\ \psi$. The probability of finding an ion at this position (to where the charge is being brought) is related to ion concentration at infinity through Boltzmann factor:

$$\frac{n_i}{n_{i\infty}} = \exp\left(-\frac{z_i e\psi}{k_B T}\right)$$

n_i is the number of ions of type i per unit volume near the surface and $n_{i\infty}$ is the concentration far from the surface, that is, the bulk concentration and z_i is the vacancy of the ion

So, we were talking about the Boltzmann factor. So, this essentially tells you what is the work that is required to bring an ion of a specific type from infinity to. So, now, if you look at this expression. So, the work that one has to do depends on what is a local psi? That means, we know that you know psi varies in a particular way, if I look at some position here and some position here or some position very very far away for example.

So, that means I would have to spend less work to bring an ion to this location, but however, if I want to go closer to this, you know, to the charge surface, because of the fact that psi is going to be higher psi is going to be highest at the surface that is psi not. Therefore, if I want to move any ion to a location much closer to the charge surface, I would have to do more work.

And so, this quantity is esentially telling you what is the probability of finding an ion at this position, at any location that I am looking at, what is the probability of finding an ion of that type at a particular location is what this quantity essentially gives you. Where n i is the number of ions per unit volume, at any location. Need not been near the surface if at any location in the vicinity of the charged surface, and n i infinity is the concentration of ions far away from the surface.

That is, you can think about if I have added if I have taken a charge surface, and say it is positive or negatively charged, if I have added say 1 milli molar salt concentration to the solution, this n i you know n I infinity can be considered as the bulk concentration, it can be considered as the concentration of the electrolyte that I have added. And z i of course is the valency of the ions. So, depending upon whether you are talking about you know, monovalent ions or divalent ions and you know z i can be, + 1 or – 1 or + 2 or – 2 depending upon you know, what kind of ions that you are working with.

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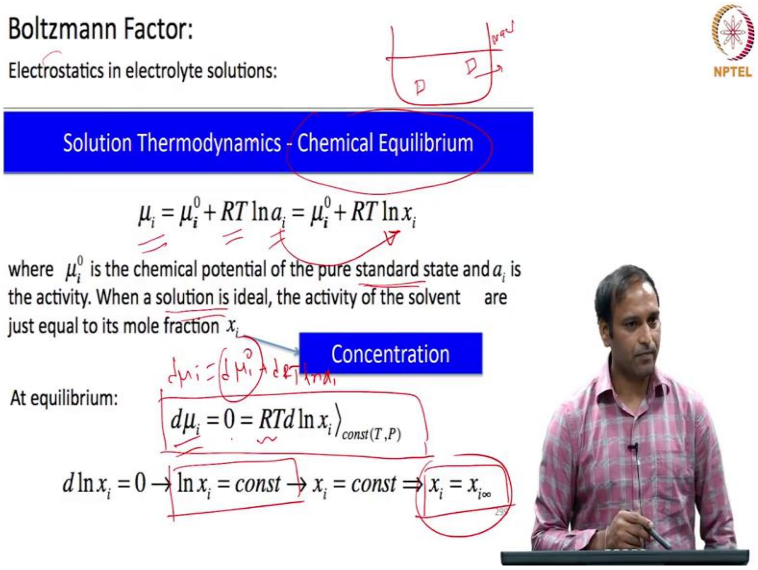

Boltzmann Factor:

Electrostatics in electrolyte solutions:

Solution Thermodynamics - Chemical Equilibrium

$$\mu_i = \mu_i^0 + RT\ln a_i = \mu_i^0 + RT\ln x_i$$

where μ_i^0 is the chemical potential of the pure standard state and a_i is the activity. When a solution is ideal, the activity of the solvent are just equal to its mole fraction x_i

Concentration

$d\mu_i = d\mu_i^0 + dRT\ln a_i$

At equilibrium:

$$\boxed{d\mu_i = 0 = RTd\ln x_i\rangle_{const(T,P)}}$$

$$d\ln x_i = 0 \rightarrow \boxed{\ln x_i = const} \rightarrow x_i = const \Rightarrow \boxed{x_i = x_{i\infty}}$$

So, you can actually think about this Boltzmann factor, you can actually derive an expression from Boltzmann factor if you know a little bit about you know, chemical equilibria of electrolyte solutions. So, we know that in solution thermodynamics, we talk about chemical equilibrium mu i which is the chemical potential is equal to mu i 0, which is the chemical potential of any species or any chemical in the standard state.

+ RT ln a i, where a i is what is called as activity coefficient. Now, when you are working with ideal solution, you can replace activity coefficient with you know, mole fraction or molar concentration of you know, ions in solution therefore, mu i becomes mu i not + RT ln x i. Now, the condition for you know, a solution to be in a thermodynamic equilibrium is that d mu i is going to be 0.

Therefore, so a d mu i is going to be df mu i 0 + dF RT ln x i. And because d mu i 0 is the chemical potential in the standard state, that is going to be 0 therefore d mu i becomes RT into d because you know, if I am working with the constant temperature I can take RT out. So, d mu i essentially becomes RT d ln x i. So, which essentially tells you that and because of the fact that you know this chemical potential is 0.

Therefore RT d ln x i = 0 or d ln x i = 0 which tells you that you know this ln of xi should be constant which gives you that x i = x i infinity that means, if for any solution to be in chemical equilibrium, the concentration of species at any location is same everywhere. That means if I have a container and like say for example, I have NaCl for example, of course this is an ionic state but I know I can take a mixture of 2 species for example.

That means, if I go to some location I look at the concentration of say species A and B in 1 location and if I look at the concentration of A and B in another location, the concentration here and here is going to be exactly same. That is what this expression essentially tells you. That is when you talk about chemical equilibrium.

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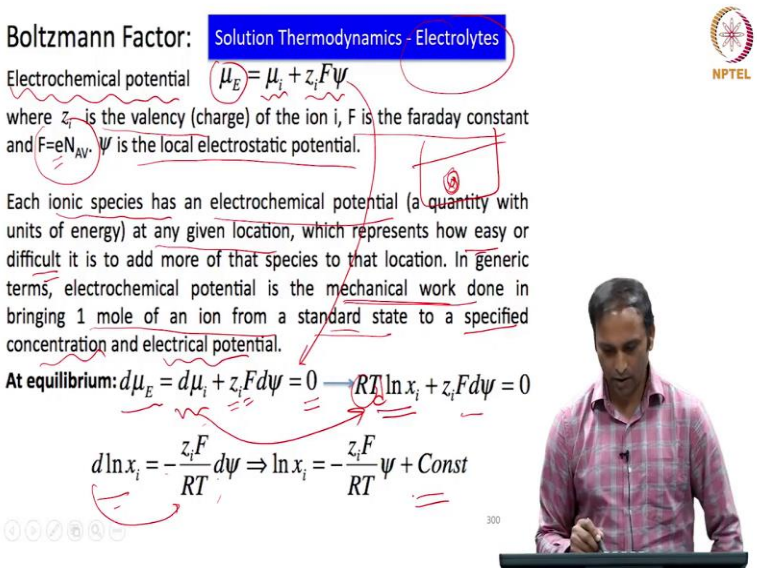

Boltzmann Factor: Solution Thermodynamics - Electrolytes

Electrochemical potential $\mu_E = \mu_i + z_i F\psi$

where z_i is the valency (charge) of the ion i, F is the faraday constant and $F=eN_{AV}$. ψ is the local electrostatic potential.

Each ionic species has an electrochemical potential (a quantity with units of energy) at any given location, which represents how easy or difficult it is to add more of that species to that location. In generic terms, electrochemical potential is the mechanical work done in bringing 1 mole of an ion from a standard state to a specified concentration and electrical potential.

At equilibrium: $d\mu_E = d\mu_i + z_i F d\psi = 0 \longrightarrow RT \ln x_i + z_i F d\psi = 0$

$$d\ln x_i = -\frac{z_i F}{RT} d\psi \Rightarrow \ln x_i = -\frac{z_i F}{RT}\psi + Const$$

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However what we are looking at is a case where you have charged species, when we talk about charged species I have an electrolyte solution, similar to chemical potential, you can define something called as a electrochemical potential. Which is mu E, that is the electrochemical potential, which is summation of the contribution that comes from the chemical potential plus an additional term.

In this additional term again z i is the valency of the ions, F is what is called as the Faraday constant and psi is what is called as a local electrostatic potential. And this Faraday constant is equal to the charge of the electron multiplied by N_{AV}, that N_{AV} is the Avogadro number. So, therefore, when you talk about electrochemical potential you can say that there is for each ionic species in solution, there is a electrochemical potential at any given location.

It depends on you know the constituents of the electrolytes at any given location in the solution there is a electrostatic potential which tells you something about how easy or how difficult it is to add more of that species into the solution at that location. Or the other way of thinking about this would be that if I want to add a particular species into a particular location, in this in the electrolyte solution, I would have to do some mechanical work.

And that mechanical work which is required to bring 1 mole of an ion from a standard state to a specified concentration and a chemical potential. That means if I have a solution, and if I want to add some species at that location. So, the amount of work that I have to do depends on what is the local concentration of ions at that location and what is the electrochemical potential because of the charge species of a particular ion that is present at that location.

So, again, of course at a chemical you know, if you say that there is something if the solution as a whole is in electrochemical equilibrium, again d mu i should be equal to 0 that means, I mix some electrolyte in solution and waited for enough time, let the system equilibrate at equilibrium, d mu E is going to be 0 therefore, d mu i + z i into F into d psi is going to be 0. This d mu i we have already shown that it is RT d ln x i.

From the previous case, + z i F d psi = 0. Therefore, I can write d ln x i. If I take this term to the hand side, so, – z i F divided by RT, RT times d psi. Therefore, I can just say If I integrate this out I get ln of x i = – z i F by RT into psi plus constant.

$$d\mu_E = d\mu_i + z_i F d\Psi = 0$$

$$\Rightarrow \ \mathrm{RT}\ \ln x_i + z_i F d\Psi = 0$$

$$\mathrm{d}\ \ln x_i = -\frac{z_i F}{RT} d\Psi \Rightarrow \ln x_i = -\frac{z_i F}{RT}\Psi + Const$$

$$x_i = x_{i\infty} exp\left(-\frac{z_i F}{RT}\Psi\right)$$

$$x_i = x_{i\infty} exp\left(-\frac{z_i e N_{AV}}{RT}\Psi\right)$$

$$x_i = x_{i\infty} exp\left(-\frac{z_i e}{k_B T}\Psi\right)$$

$$Where, \qquad k_B = \left(\frac{R}{N_{AV}}\right)$$

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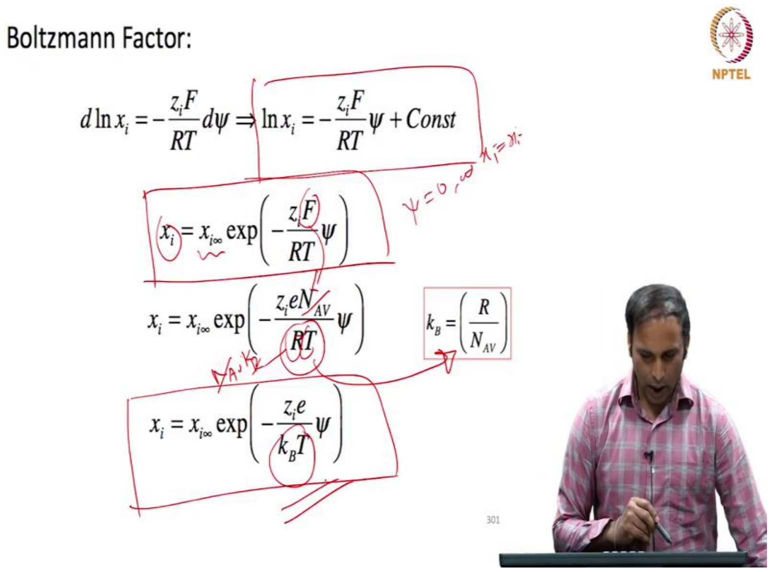

Boltzmann Factor:

$$d\ln x_i = -\frac{z_iF}{RT}d\psi \Rightarrow \ln x_i = -\frac{z_iF}{RT}\psi + Const$$

$\psi = 0, \infty \; x_i = x_{i\infty}$

$$x_i = x_{i\infty}\exp\left(-\frac{z_iF}{RT}\psi\right)$$

$$x_i = x_{i\infty}\exp\left(-\frac{z_ieN_{AV}}{RT}\psi\right) \qquad k_B = \left(\frac{R}{N_{AV}}\right)$$

$N_A k_B$

$$x_i = x_{i\infty}\exp\left(-\frac{z_ie}{k_BT}\psi\right)$$

That is what you get and of course, if I substitute the limits that you know at psi is going to be 0 at x i = x i infinity you know if I do all of that, so, therefore, I get an expression which lets x i which is the concentration of a particular ionic species, at any given location, you know is equal to x i infinity, which is the concentration of the same species at infinity times exponent of – z i, F by RT into psi.

And, and we know that F is e times N_{AV}. We are substituting for F as e times N_{AV} and RT is related to the Boltzmann constant as R = k_B times N_{AV}. So, if I replace instead of R, if I put N_{AV} times k_B, this N_{AV} gets cancelled. Therefore, I have k_BT in the denominator and z i into e is in the numerator. Therefore, x i essentially is equal to x i infinity into exponent – z i e divided by k_BT times psi.

So, this essentially is the Boltzmann factor. So, either you can define it or you can actually go through this route of electrochemical potential and invoke the fact that when you have an electrolyte solution in equilibrium, the electrochemical potential is 0 and you can actually essentially derive the Boltzmann factor.

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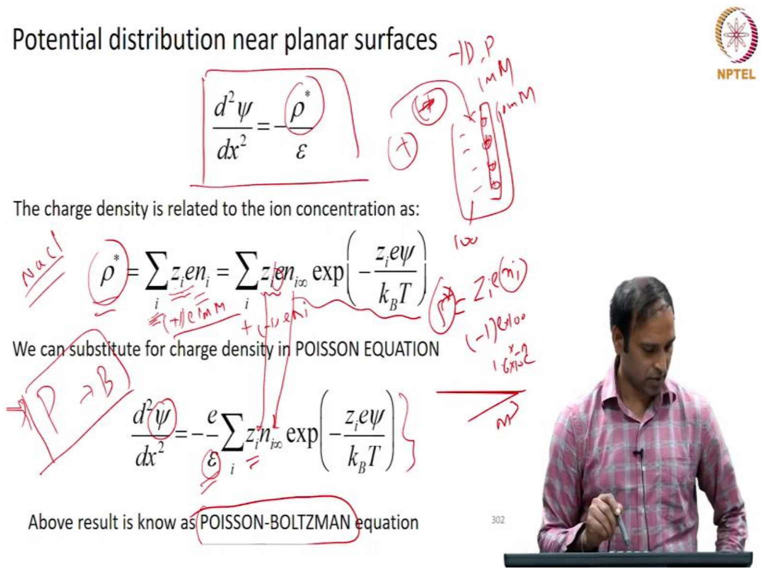

Potential distribution near planar surfaces

$$\frac{d^2\psi}{dx^2} = -\frac{\rho^*}{\varepsilon}$$

The charge density is related to the ion concentration as:

$$\rho^* = \sum_i z_i e n_i = \sum_i z_i e n_{i\infty} \exp\left(-\frac{z_i e\psi}{k_B T}\right)$$

We can substitute for charge density in POISSON EQUATION

$$\frac{d^2\psi}{dx^2} = -\frac{e}{\varepsilon}\sum_i z_i n_{i\infty} \exp\left(-\frac{z_i e\psi}{k_B T}\right)$$

Above result is know as POISSON-BOLTZMAN equation

So, that is what we have. So, we would like to solve this 1 D Poisson equation you would like to solve that. This rho star is summation of summation z i e n i because, you know, I would have to you know, I could have a you know case where I have a charged species, you know, it is not necessary that if I have a charge species I said that, you should always think about counter ions being in solution.

This is the most ideal case. I only have the charge surface and the counters which come only because of dissociation of charges on the particle surface. However, in general, so, if I have a case like this, my rho star is only going to be just z i e n i, that is it. In this case, the counter ions being negative, so it is going to be – 1 times e and n i is going to be the concentration of ions in solution.

If I say that there are 100 you know ions for example, is going to be multiplied by 100 multiplied by 1.6 into 10 to power –19 coulomb divided by the volume of the solution that gives me what is rho star. This is the charge density, the charge per unit volume, that is how you get rho star but however, in several cases, what you will do is you will have counter ions because of the dissociation plus additionally we will also add a lot of salt.

You always hear terms like you know, I have a choice stabilized dispersion I have added 1 milli molar salt to the dispersion or I have added 10 milli molar salt to dispersion. When you have a case like this, I would have both co-ions as well as counter-ions in solution. Therefore, if you want to calculate rho star, I would have to sum up all the ions present. That is summation of z, for example, if I have NaCl for example, only NaCl.

Then what are we going to have is for Na is going to be + 1 times e, again the concentration of the concentration is say 1 milli molar. For example 1 milli molar divided by, of course you to convert a number by using, you know, have a Avogadro number all that. But anyway plus, I would have – 1 that is because of Cl –, plus multiply by e n i. So therefore, this rho star, you would have sum up all the ions present in the solution both co ions, counter ions.

You could have case where there could be multiple, you know, ions present to the solution. I would have to sum all of them up. This rho star has given as sigma i z i times e times n i. Now, z i e I am going to keep it the way it is and the for n i, I am going to substitute for the Boltzmann factor. And because e and epsilon, if I am working with a particular solution I mean, if the dielectric constant the medium that I am using is like say for example water you know to particular conditions.

I can you know, your epsilon is essentially going to be constant. So, I can take – e divided by epsilon out sigma I have z i, I have n i infinity exponent – z i e psi divided by $k_B T$. This expression is what is called as a Poisson Boltzmann equation. Because we started with the Poisson equation and then we use a Boltzmann factor. You know, and then we obtain an expression for how does the potential vary as a function of you know, a differential equation. That counts the variation of the potential as a function of separation distance. That is what is called the Poisson Boltzmann equation.