

DERIVATION OF THE DEBYE-HUCKEL EQUATION FOR STRONG ELECTROLYTES

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ESTABLISHING THE DEBYE-HUCKEL POTENTIAL

Strong electrolytes are entirely dissociated, *i.e.*, NaCl. Ions will be considered as hard spheres that are distributed in a continuum of dielectric constant ϵ_0 , the solvent water, and yielding an average charge density ρ_e .

The Poisson equation states that the potential is given by:

$$\nabla^2 \phi = \frac{-4\pi}{\epsilon_0} \rho_e \quad (1)$$

Therefore, an ion will feel the electrical potential created by the other ions according to the above equation. Because of the spherical nature of the ions, it is best to use polar coordinates to express the Poisson equation. Hence,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) = \frac{-4\pi}{\epsilon_0} \rho_e \quad (2)$$

With s ions of charge z_i for ion i . Electroneutrality implies:

$$\sum_{i=1}^{i=s} n_i z_i = 0 \quad (3)$$

Isolating ion J as a central ion, the objective is to determine the effect of all the other ions on J, and sum up the result over all other ions. This will yield the electrical potential energy that we will relate in a second step to the chemical potential and consequently the activity coefficients for individual ions.

We need to define a distance of closest approach, a_D , between the central ion J and a counter ion Cl.

$$a_D = r_J + r_{Cl} \quad (4)$$

where r_J = radius of ion J and r_{Cl} = radius of the counter ion.

The electroneutrality of the solution entails that the summation of all charges around the central ion must be equal to the charge bore by the central ion J. Hence,

$$\int_{a_D}^{\infty} 4\pi r^2 \rho_e dr = -z_J e \quad (5)$$

With no electrical interactions, the average distribution of ions of type i is simply n_i , that is the number of ions per unit volume of solution. In this case particles interact electrostatically, therefore Debye-Huckel used the Boltzmann distribution function instead. Hence,

$$n'_i = n_i \exp\left(\frac{-E_e}{k_B T}\right) \quad (6)$$

where k_B is the Boltzmann constant.

This is related to the probability of finding an ion i per volume element at the center of which the electrical potential energy is E_e . Note that when $E_e = 0$, then it results in a uniform distribution. In our case,

$$E_e = z_i e \phi_J \quad (7)$$

and

$$n'_i = n_i \exp\left(\frac{-z_i e \phi_J}{k_B T}\right) \quad (8)$$

The thermal energy with increasing temperature smears out the distribution. This distribution function gives the probability of finding an ion i per volume element (it is therefore concentration related) at a distance r_J from the central ion. Now, we can just sum up this result over all other ions to express the charge density with respect to the central ion J .

$$\rho_J = \sum n_i z_i e \exp\left(\frac{-z_i e \phi_J}{k_B T}\right) \quad (9)$$

The Poisson equation then becomes:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi_J}{dr} \right) = \frac{-4\pi}{\epsilon_0} \sum n_i z_i e \exp\left(\frac{-z_i e \phi_J}{k_B T}\right) \quad (10)$$

In order to solve this equation, Debye-Huckel made a **very important simplifying assumption**. On the grounds that $z_i e \phi_J \ll k_B T$, or that the energy derived from electrical forces is small compared to the thermal energy, they expanded the exponential term in power series and neglected higher order terms, *i.e.*, terms of degree 2 and higher. Given that:

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots \quad (11)$$

one obtains:

$$\rho_J = \sum n_i z_i e - \sum n_i z_i e \left(\frac{z_i e \phi_J}{k_B T} \right) \quad (12)$$

Since the first term is equal to zero, because of the electroneutrality condition, one finally gets:

$$\rho_J = - \sum \frac{n_i z_i^2 e^2 \phi_J}{k_B T} \quad (13)$$

Therefore,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) = \frac{4\pi}{\varepsilon_0} \sum \frac{n_i z_i^2 e^2 \phi_J}{k_B T} \quad (14)$$

or

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) = \frac{4\pi e^2}{\varepsilon_0 k_B T} \sum n_i z_i^2 \phi_J \quad (15)$$

or, in a simpler manner:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) = \kappa^2 \phi_J \quad (16)$$

where

$$\kappa^2 = \frac{4\pi e^2}{\varepsilon_0 k_B T} \sum n_i z_i^2 \quad (17)$$

It turns out that κ is in reciprocal length (L^{-1}). A general solution of equation (16) that satisfies the fact that the potential remains finite when $r \rightarrow \infty$ is:

$$\phi_J = \frac{A}{r} e^{-\kappa r} \quad (18)$$

To obtain the value of the constant A, we need to state the electroneutrality of the solution. Therefore, using equations (9), (17), and (18) leads to :

$$\rho_J = \frac{-\kappa^2 \varepsilon_0}{4\pi} A \frac{e^{-\kappa r}}{r} \quad (19)$$

Using this equation in the expression of ρ_J , we can write a new expression for the electroneutrality, using (5), one gets:

$$A \kappa^2 \varepsilon_0 \int_{a_D}^{\infty} r e^{-\kappa r} dr = z_J e \quad (20)$$

after an integration by parts, one obtains the value of the constant A:

$$A = \frac{z_J e}{\varepsilon_0} \frac{e^{\kappa a_D}}{1 + \kappa a_D} \quad (21)$$

Hence the expression of the potential is:

$$\phi_J = \frac{z_J e}{\varepsilon_0} \frac{e^{\kappa a_D}}{1 + \kappa a_D} \frac{e^{-\kappa r}}{r} \quad (22)$$

This gives the expression of the potential at a distance r from the central ion J. The Poisson equation is only valid for static charges, this is not the case in solution. But we shall say that, since we are dealing with time averaged positions of the ions this assumption will hold.

The potential due to ion J at a distance r from its center is

$$\phi_J'' = \frac{z_J e}{\epsilon_0 r} \quad (23)$$

The total potential at a distance r is

$$\phi_J = \phi_J' + \phi_J'' \quad (24)$$

Then,

$$\phi_J' = \frac{z_J e}{\epsilon_0 r} \left(\frac{e^{\kappa a_D}}{1 + \kappa a_D} e^{-\kappa r} - 1 \right) \quad (25)$$

The potential due to all the other ions upon the surface of the central ion J is simply:

$$\phi_J' = \frac{z_J e}{\epsilon_0} \left(\frac{\kappa}{1 + \kappa a_D} \right) \quad (26)$$

and if $a_D \ll \frac{1}{\kappa}$, like it is the case in a dilute solution, one gets:

$$\phi_J' = \frac{z_J e}{\epsilon_0} \kappa \quad (27)$$

We can now calculate the change in electrical free energy of the solution at constant temperature and pressure when an ion J is added to the solution.

$$\Delta G_J = -z_J e \phi_J' \quad (28)$$

or

$$\Delta G_J = \frac{z_J^2 e^2}{2\epsilon_0} \left(\frac{\kappa}{1 + \kappa a_D} \right) \quad (29)$$

The number 2 occurs in the denominator because when all ions are considered J is counted twice. It is counted as the central ion and also as part of the atmosphere of other ions. We can relate now this change in free energy to the chemical potential. Assuming that 1 mole of ion is added to a large volume of solution, one obtains:

$$\Delta \mu_{e,J} = \frac{z_J^2 e^2 \mathcal{N}}{2\epsilon_0} \left(\frac{\kappa}{1 + \kappa a_D} \right) \quad (30)$$

Considering that μ has two contributions: $\mu_J = \mu_{ideal} + \Delta \mu_{e,J}$ and that $\mu_J = \mu_J^o + RT \ln \gamma_J + RT \ln [J]$ we obtain

$$\ln \gamma_J = \frac{z_J^2 e^2}{2\epsilon_0 k_B T} \left(\frac{\kappa}{1 + \kappa a_D} \right) \quad (31)$$

REFERENCE

Robinson R. A., and R. H. Stokes (1968) *Electrolytes Solutions*, Butterworths, London.