10.5: Derivation of the Debye-Hückel Theory

Debye and Hückel derived Eq. 10.4.1 using a combination of electrostatic theory, statistical mechanical theory, and thermodynamics. This section gives a brief outline of their derivation.

The derivation starts by focusing on an individual ion of species i as it moves through the solution; call it the central ion. Around this central ion, the time-average spatial distribution of any ion species j is not random, on account of the interaction of these ions of species j with the central ion. (Species i and j may be the same or different.) The distribution, whatever it is, must be spherically symmetric about the central ion; that is, a function only of the distance r from the center of the ion. The local concentration, c_j', of the ions of species j at a given value of r depends on the ion charge $z_j e$ and the electric potential ϕ at that position. The time-average electric potential in turn depends on the distribution of all ions and is symmetric about the central ion, so expressions must be found for c_j' and ϕ as functions of r that are mutually consistent.

Debye and Hückel assumed that c_j' is given by the Boltzmann distribution

$$c_j' = c_j e^{-z_j e\phi/kT} \tag{10.5.1}$$

where $z_j e\phi$ is the electrostatic energy of an ion of species j, and k is the Boltzmann constant ($k = R/N_A$). As r becomes large, ϕ approaches zero and c_j' approaches the macroscopic concentration c_j. As T increases, c_j' at a fixed value of r approaches c_j because of the randomizing effect of thermal energy. Debye and Hückel expanded the exponential function in powers of $1/T$ and retained only the first two terms: $c_j' \approx c_j(1 - z_j e\phi/kT)$. The distribution of each ion species is assumed to follow this relation. The electric potential function consistent with this distribution and with the electroneutrality of the solution as a whole is

$$\phi = (z_i e/4\pi\epsilon_r\epsilon_0 r)e^{\kappa(a-r)}/(1+\kappa a) \tag{10.5.2}$$

Here κ is defined by $\kappa^2 = 2N_A^2 e^2 I_c/\epsilon_r\epsilon_0 RT$, where I_c is the *ionic strength on a concentration basis* defined by $I_c = (1/2)\sum_i c_i z_i^2$.

The electric potential ϕ at a point is assumed to be a sum of two contributions: the electric potential the central ion would cause at infinite dilution, $z_i e/4\pi\epsilon_r\epsilon_0 r$, and the electric potential due to all other ions, ϕ'. Thus, ϕ' is equal to $\phi - z_i e/4\pi\epsilon_r\epsilon_0 r$, or

$$\phi' = (z_i e/4\pi\epsilon_r\epsilon_0 r)[e^{\kappa(a-r)}/(1+\kappa a) - 1] \tag{10.5.3}$$

This expression for ϕ' is valid for distances from the center of the central ion down to a, the distance of closest approach of other ions. At smaller values of r, ϕ' is constant and equal to the value at $r = a$, which is $\phi'(a) = -(z_i e/4\pi\epsilon_r\epsilon_0)\kappa/(1+\kappa a)$. The interaction energy between the central ion and the surrounding ions (the ion atmosphere) is the product of the central ion charge and $\phi'(a)$.

The last step of the derivation is the calculation of the work of a hypothetical reversible process in which the surrounding ions stay in their final distribution, and the charge of the central ion gradually increases from zero to its actual value $z_i e$. Let $\alpha z_i e$ be the charge at each stage of the process, where α is a fractional advancement that changes from 0 to 1. Then the work w' due to the interaction of the central ion with its ion atmosphere is $\phi'(a)$ integrated over the charge:

$$
\begin{aligned}
w' &= -\int_{\alpha=0}^{\alpha=1} [(\alpha z_i e/4\pi\epsilon_r\epsilon_0)\kappa/(1+\kappa a)]\,\mathrm{d}(\alpha z_i\epsilon) \\
&= -(z_i^2 e^2/8\pi\epsilon_r\epsilon_0)\kappa/(1+\kappa a)
\end{aligned}
\tag{10.5.4}
$$

Since the infinitesimal Gibbs energy change in a reversible process is given by $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + đw'$ (Eq. 5.8.6), this reversible nonexpansion work at constant T and p is equal to the Gibbs energy change. The Gibbs energy change per amount of species i is $w'N_A = -(z_i^2 e^2 N_A/8\pi\epsilon_r\epsilon_0)\kappa/(1+\kappa a)$. This quantity is $\Delta G/n_i$ for the process in which a solution of fixed composition changes from a hypothetical state lacking ion–ion interactions to the real state with ion–ion interactions present. $\Delta G/n_i$ may be equated to the difference of the chemical potentials of i in the final and initial states. If the chemical potential without ion–ion interactions is taken to be that for ideal-dilute behavior on a molality basis, $\mu_i = \mu_{m,i}^{\mathrm{ref}} + RT\ln(m_i/m^\circ)$, then $-(z_i^2 e^2 N_A/8\pi\epsilon_r\epsilon_0)\kappa/(1+\kappa a)$ is equal to $\mu_i - [\mu_{m,i}^{\mathrm{ref}} + RT\ln(m_i/m^\circ)] = RT\ln\gamma_{m,i}$. In a dilute solution, c_i can with little error be set equal to $\rho_A^* m_i$, and I_c to $\rho_A^* I_m$. Equation 10.4.1 follows.