Debye–Hückel equation

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(Redirected from Debye-Hückel equation)

The **Debye–Hückel equation** and **Debye–Hückel limiting law**, were derived by Peter Debye and Erich Hückel, who developed a theory with which to calculate activity coefficients of electrolyte solutions.[1] Activities, rather than concentrations, are needed in many chemical calculations because solutions that contain ionic solutes do not behave ideally even at very low concentrations. The activity is proportional to the concentration by a factor known as the activity coefficient γ, and takes into account the interaction energy of ions in the solution.

When combining this result for the charge density with the Poisson equation from electrostatics, a form of the Poisson-Boltzmann equation results:[1]:233

$$\nabla^2\varphi = -\frac{\rho}{\varepsilon_r\varepsilon_0} = -\sum_i \frac{z_i q n_i^0}{\varepsilon_r\varepsilon_0} e^{-\frac{z_i q\varphi}{k_B T}}.$$

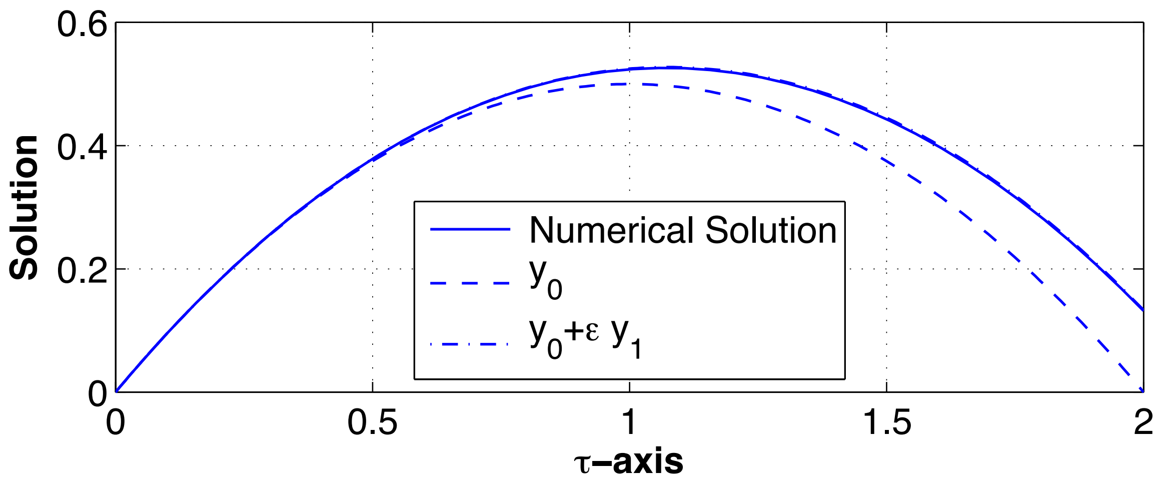
This equation is difficult to solve and does not follow the principle of linear superposition for the relationship between the number of charges and the strength of the potential field. However, for sufficiently low concentrations of ions, a first order Taylor series approximation for the exponential function may be used ($e^x = 1 + x$ for $0 < x \ll 1$) to create a linear differential equation (Hamann, Hamnett, and Vielstich. Electrochemistry. Wiley-VCH. section 2.4.2). D&H say that this approximation holds at large distances between ions,[1]:227 which is the same as saying that the concentration is low. Lastly, they claim without proof that the addition of more terms in the expansion has little effect on the final solution.[1]:227 Thus,

$$-\sum_i \frac{z_i q n_i^0}{\varepsilon_r\varepsilon_0} e^{-\frac{z_i q\varphi}{k_B T}} \approx -\sum_i \frac{z_i q n_i^0}{\varepsilon_r\varepsilon_0}\left(1 - \frac{z_i q\varphi}{k_B T}\right) = -\left(\sum_i \frac{z_i q n_i^0}{\varepsilon_r\varepsilon_0} - \sum_i \frac{z_i^2 q^2 n_i^0\varphi}{\varepsilon_r\varepsilon_0 k_B T}\right)$$

.

The Poisson-Boltzmann equation is transformed to[1]:233

$$\nabla^2\varphi = \sum_i \frac{z_i^2 q^2 n_i^0\varphi}{\varepsilon_r\varepsilon_0 k_B T},$$



0.6
0.4
0.2
0
Solution
0
0.5
1
1.5
2
τ−axis
Numerical Solution
y0
y0+ε y1