

## 16.18: Activities of Electrolytes - The Debye-Hückel Theory

In earlier sections, we introduce some basic methods for the experimental measurement of activities and activity coefficients. The Debye-Hückel theory leads to an equation for the activity coefficient of an ion in solution. The theory gives accurate values for the activity of an ion in very dilute solutions. As salt concentrations become greater, the accuracy of the Debye-Hückel model decreases. As a rough rule of thumb, the theory gives useful values for the activity coefficients of dissolved ions in solutions whose total salt concentrations are less than about 0.01 molal.<sup>2</sup> The theory is based on an electrostatic model. We describe this model and present the final result. We do not, however, present the argument by which the result is obtained.

We begin by reviewing some necessary ideas from electrostatics. When point charges  $q_1$  and  $q_2$  are embedded in a continuous medium, the Coulomb's law force exerted on  $q_1$  by  $q_2$  is

$$\vec{F}_{21} = \frac{q_1 q_2 \hat{r}_{21}}{4\pi\epsilon_0 D r_{12}^2}$$

where  $\epsilon_0$  is a constant called the permittivity of free space, and  $D$  is a constant called the **dielectric coefficient** of the continuous medium.  $\hat{r}_{21}$  is a unit vector in the direction from the location of  $q_2$  to the location of  $q_1$ . When  $q_1$  and  $q_2$  have the same sign, the force is positive and acts to increase the separation between the charges. The force exerted on  $q_2$  by  $q_1$  is  $\vec{F}_{12} = -\vec{F}_{21}$ ; the net force on the system of charges is

$$\vec{F}_{net} = \vec{F}_{12} + \vec{F}_{21} = 0.$$

When the force is expressed in newtons, the point charges are expressed in coulombs, and distance is expressed in meters,  $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$ . The dielectric coefficient is a dimensionless quantity whose value in a vacuum is unity. In liquid water at 25 °C,  $D = 78.4$ . We are interested in the interactions between ions whose charges are multiples of the fundamental unit of charge,  $e$ . We designate the charge on a proton and an electron as  $e$  and  $-e$ , respectively, where  $e = 1.602 \times 10^{-19} \text{ C}$ . We express the charge on a cation, say  $A^{m+}$ , as  $z_A e$ , and that on an anion, say  $B^{n-}$ , as  $z_B e$ , where  $z_A = +m > 0$  and  $z_B = -n < 0$ .

The Debye-Hückel theory models the environment around a particular central ion—the ion whose activity coefficient we calculate. We assume that the interactions between the central ion and all other ions result exclusively from Coulomb's law forces. We assume that the central ion is a hard sphere whose charge,  $q_C$ , is located at the center of the sphere. We let the radius of this sphere be  $a_C$ . Focusing on the central ion makes it possible to simplify the mathematics by fixing the origin of the coordinate system at the center of the central ion; as the central ion moves through the solution, the coordinate system moves with it. The theory develops a relationship between the activity coefficient of the central ion and the electrical work that is done when the central ion is brought into the solution from an infinite distance—where its potential energy is taken to be zero.

The theory models the interactions of the central ion with the other ions in the solution by supposing that, for every type of ion,  $k$ , in the solution, there is a spherically symmetric function,  $\rho_k(r)$ , which specifies the concentration of  $k$ -type ions at the location specified by  $r$ , for  $r \geq a_C$ . That is, we replace our model of mobile point-charge ions with a model in which charge is distributed continuously. The physical picture corresponding to this assumption is that the central ion remains discrete while all of the other ions are “ground up” into tiny charged bits that are spread smoothly—but not uniformly—throughout the solution that surrounds the central ion. The introduction of  $\rho_k(r)$  changes our model from one involving point-charge neighbor ions—whose effects would have to be obtained by summing an impracticably large number of terms and whose locations are not well defined anyway—to one involving a mathematically continuous function. From this perspective, we adopt, for the sake of a quantitative mathematical treatment, a physical model that violates the atomic description of everything except the central ion.

It is useful to have a name for the collection of charged species around the central ion; we call it the **ionic atmosphere**. The ionic atmosphere occupies a microscopic region around the central ion in which ionic concentrations depart from their macroscopic-solution values. The magnitudes of these departures depend on the sign and magnitude of the charge on the central ion.

The essence of the Debye-Hückel model is that the charge of the central ion gives rise to the ionic atmosphere. To appreciate why this is so, we can imagine introducing an uncharged moiety, otherwise identical to the central ion, into the solution. In such a process, no ionic atmosphere would form. As far as long-range Coulombic forces are concerned, no work would be done.

When we imagine introducing the charged central ion into the solution in this way, Coulombic forces lead to the creation of the ionic atmosphere. Since formation of the ionic atmosphere entails the separation of charge, albeit on a microscopic scale, this

process involves electrical work. Alternatively, we can say that electrical work is done when a charged ion is introduced into a salt solution and that this work is expended on the creation of the ionic atmosphere.

In the Debye-Hückel model, this electrical work is the energy change associated with the process of solvating the ion. Since the reversible, non-pressure-volume work done in a constant-temperature, constant-pressure process is also the Gibbs free energy change for that process, the work of forming the ionic atmosphere is the same thing as the Gibbs free energy change for introducing the ion into the solution.

The Debye-Hückel theory makes these ideas quantitative by finding the work done in creating the ionic atmosphere. To do this, it proves to be useful to define a quantity that we call the **ionic strength** of the solution. By definition, the ionic strength is

$$I = \sum_{k=1}^n z_k^2 m_k / 2$$

where the sum is over all of the ions present in the solution. The factor of  $1/2$  is essentially arbitrary. We introduce it in order to make the ionic strength of a 1:1 electrolyte equal to its molality. ( $z_k$  is dimensionless.)

For the hypothetical one-molal standard state that we consider in §6, the activity coefficient for solute  $C$ ,  $\gamma_C$ , is related to the chemical potential of the real substance,  $\mu_C(P, \underline{m}_C)$ , and that of a hypothetical ideal solute  $C$  at the same concentration,  $\mu_C(\text{Hyp solute}, P, \underline{m}_C)$ , by

$$\ln \gamma_C = \frac{\mu_C(P, \underline{m}_C) - \mu_C(\text{Hyp solute}, P, \underline{m}_C)}{RT}$$

The Debye-Hückel model equates this chemical-potential difference to the electrical work that accompanies the introduction of the central ion into a solution whose ionic strength is  $I$ . The final result is

$$\ln \gamma_C = \frac{-z_C^2 e^2 \bar{\kappa} \bar{N}}{8\pi \epsilon_0 D (1 + \kappa a_C)}$$

(While it is not obvious from our discussion, the parameter,

$$\kappa = \left( \frac{2e^2 \bar{N} d_w I}{\epsilon_0 D k T} \right)^{1/2}$$

characterizes the ionic atmosphere around the central ion. The quantity  $d_w$  is the density of the pure solvent, which is usually water.)

For sufficiently dilute solutions,  $1 + \kappa a_C \approx 1$ . (See problem 14.) Introducing this approximation, substituting for  $\kappa$ , and dividing by 2.303 to convert to base-ten logarithms, we obtain the **Debye-Hückel limiting law** in the form in which it is usually presented:

$$\log_{10} \gamma_C = -A_\gamma z_C^2 I^{1/2}$$

where

$$A_\gamma = \frac{(2d_w)^{1/2} \bar{N}^2}{2.303 (8\pi)} \left( \frac{e^2}{\epsilon_0 D R T} \right)^{3/2}$$

For aqueous solutions at 25 C,  $A_\gamma = 0.510$ .

The Debye-Hückel model finds the activity of an individual ion. In §18, we note that the activity of an individual ion cannot be determined experimentally. We introduce the mean activity coefficient,  $\gamma_\pm$ , for a strong electrolyte as a way to express the departure of a salt solution from ideal-solution behavior. Adopting the hypothetical one-molal ideal-solution state as the standard state for the salt,  $A_p B_q$ , we develop conventions that express the Gibbs free energy of a real salt solution and find

$$\gamma_\pm = (\gamma_A^p \gamma_B^q)^{1/(p+q)}.$$

Using the Debye-Hückel limiting law values for the individual-ion activity coefficients, we find

$$\log_{10} \gamma_{\pm} = \frac{p \log_{10} \gamma_A + q \log_{10} \gamma_B}{p + q} = \frac{-p A_{\gamma} z_A^2 I^{1/2} - q A_{\gamma} z_B^2 I^{1/2}}{p + q} = - \left( \frac{p z_A^2 + q z_B^2}{p + q} \right) A_{\gamma} I^{1/2} = -A_{\gamma} z_A z_B I^{1/2}$$

where we use the identity

$$\frac{p z_A^2 + q z_B^2}{p + q} = -z_A z_B$$

(See problem 16.12.)

---

This page titled [16.18: Activities of Electrolytes - The Debye-Hückel Theory](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Paul Ellgen](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.