\newcommand{\tx}[1]{\text{#1}} % text in math mode
\newcommand{\subs}[1]{{_{\text{#1}}}} % subscript text
\newcommand{\sup}[1]{{^{\text{#1}}}} % superscript text
\newcommand{\st}{{^\circ}} % standard state symbol
\newcommand{\id}{{^\text{id}}} % ideal
\newcommand{\rf}{{^\text{ref}}} % reference state
\newcommand{\units}[1]{\mbox{$\thinspace$#1}}
\newcommand{\K}{\units{K}} % kelvins
\newcommand{\degC}{{^\circ\text{C}}} % degrees Celsius
\newcommand{\br}{\units{bar}} % bar \bar is already defined
\newcommand{\Pa}{\units{Pa}} % pascal
\newcommand{\mol}{\units{mol}} % mole
\newcommand{\V}{\units{V}} % volts
\newcommand{\timesten}[1]{\mbox{$\,	imes\,10^{#1}$}}
\newcommand{\per}{^{-1}} % minus one power
\newcommand{\m}{{_{\text{m}}}} % subscript m for molar quantity
\newcommand{\CVm}{\text{C}_{V,\text{m}}} % molar heat capacity at const.V
\newcommand{\Cpm}{\text{C}_{p,\text{m}}} % molar heat capacity at const.p
\newcommand{\kT}{k_T} % isothermal compressibility
\newcommand{\A}{{_{\text{A}}}} % subscript A for solvent or state A
\newcommand{\B}{{_{\text{B}}}} % subscript B for solute or state B
\newcommand{\bd}{{_{\text{b}}}} % subscript b for boundary or boiling point
\newcommand{\C}{{_{\text{C}}}} % subscript C
\newcommand{\f}{{_{\text{f}}}} % subscript f for freezing point
\newcommand{\mA}{{_{\text{m},\text{A}}}} % subscript m,A (m=molar)
\newcommand{\mB}{{_{\text{m},\text{B}}}} % subscript m,B (m=molar)
\newcommand{\mi}{{_{\text{m},\text{i}}}} % subscript m,i (m=molar)
\newcommand{\kHi}{{k_{\text{H},\text{i}}}} % Henry's law constant, x basis, i
\newcommand{\kHB}{{k_{\text{H},\text{B}}}} % Henry's law constant, x basis, B
\newcommand{\ra}{\rightarrow} % right arrow (can be used in text mode)
\newcommand{\eq}{{\subs{eq}}} % equilibrium state
\newcommand{\onehalf}{\textstyle\frac{1}{2}\D} % small 1/2 for display equation
\newcommand{\sys}{{\subs{sys}}} % system property
\newcommand{\sur}{{\sups{sur}}} % surroundings
The theory of Peter Debye and Erich Hückel (1923) provides theoretical expressions for single-ion activity coefficients and mean ionic activity coefficients in electrolyte solutions. The expressions in one form or another are very useful for extrapolation of quantities that include mean ionic activity coefficients to low solute molality or infinite dilution.

The only interactions the theory considers are the electrostatic interactions between ions. These interactions are much stronger than those between uncharged molecules, and they die off more slowly with distance. If the positions of ions in an electrolyte solution were completely random, the net effect of electrostatic ion–ion interactions would be zero,
because each cation–cation or anion–anion repulsion would be balanced by a cation–anion attraction. The positions are not random, however: each cation has a surplus of anions in its immediate environment, and each anion has a surplus of neighboring cations. Each ion therefore has a net attractive interaction with the surrounding ion atmosphere. The result for a cation species at low electrolyte molality is a decrease of \( \mu_+ \) compared to the cation at same molality in the absence of ion–ion interactions, meaning that the single-ion activity coefficient \( \gamma_+ \) becomes less than \( 1 \) as the electrolyte molality is increased beyond the ideal-dilute range. Similarly, \( \gamma_- \) also becomes less than \( 1 \).

According to the Debye–Hückel theory, the single-ion activity coefficient \( \gamma_i \) of ion \( i \) in a solution of one or more electrolytes is given by

\[
\ln \gamma_i = -\frac{A_{DH} z_i^2 \sqrt{I_m}}{1 + B_{DH} a \sqrt{I_m}}
\tag{10.4.1}
\]

where

- \( z_i \) is the charge number of ion \( i \) (\(+1\), \(-2\), etc.);
- \( I_m \) is the ionic strength of the solution on a molality basis, defined by
  \[
  I_m \defn \frac{1}{2} \sum \text{all ions} m_j z_j^2
  \tag{10.4.2}
  \]
- \( A_{DH} \) and \( B_{DH} \) are defined functions of the kind of solvent and the temperature;
- \( a \) is an adjustable parameter, equal to the mean effective distance of closest approach of other ions in the solution to one of the \( i \) ions.

The definitions of the quantities \( A_{DH} \) and \( B_{DH} \) appearing in Eq. 10.4.1 are

\[
A_{DH} \defn \left( N_A^2 e^3 / 8 \pi \right) \left( 2 \rho A^* \right)^{1/2} \left( \epsilon_r \epsilon_0 RT \right)^{-3/2}
\tag{10.4.3}
\]
\[
B_{DH} \defn N_A e \left( 2 \rho A^* \right)^{1/2} \left( \epsilon_r \epsilon_0 RT \right)^{-1/2}
\tag{10.4.4}
\]

where \( N_A \) is the Avogadro constant, \( e \) is the elementary charge (the charge of a proton), \( \rho \) and \( \epsilon_r \) are the density and relative permittivity (dielectric constant) of the solvent, and \( \epsilon_0 \) is the electric constant (or permittivity of vacuum).

Lewis and Randall (\emph{J. Am. Chem. Soc.}, 1112–1154, 1921) introduced the term ionic strength, defined by Eq. 10.4.2, two years before the Debye–Hückel theory was published. They found empirically that in dilute solutions, the mean ionic activity coefficient of a given strong electrolyte is the same in all solutions having the same ionic strength.

When the solvent is water at 25\( \degC \), the quantities \( A_{DH} \) and \( B_{DH} \) have the values

\[
A_{DH} = 1.1744 \text{ kg}^{1/2} \text{ mol}^{-1/2}
\tag{10.4.5}
\]
\[
B_{DH} = 3.285 \times 10^9 \text{ m}^{-1} \text{ kg}^{1/2} \text{ mol}^{-1/2}
\tag{10.4.6}
\]

From Eqs. 10.3.8 and 10.4.1 and the electroneutrality condition \( \nu_+ z_+ = \nu_- z_- \), we obtain the following expression for the logarithm of the mean ionic activity coefficient of an electrolyte solute: \begin{equation}
\ln \gamma_{\pm} = -\frac{A_{DH} \left| z_+ z_- \right| \sqrt{I_m}}{1 + B_{DH} a \sqrt{I_m}}
\tag{10.4.7}
\end{equation}

In this equation, \( z_+ \) and \( z_- \) are the charge numbers of the cation and anion of the solute. Since the right side of Eq. 10.4.7 is negative at finite solute molalities, and zero at infinite dilution, the theory predicts that \( \gamma_{\pm} \) is less than \( 1 \) at finite solute molalities and approaches \( 1 \) at infinite dilution.
Figure 10.3 Mean ionic activity coefficient of aqueous HCl at 25 units\(^\circ\text{C}\). Solid curve: experiment (Herbert S. Harned and Benton B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd edition, Reinhold, New York, 1958, Table 11-5-1); dashed curve: Debye–Hückel theory with \(a = 5 \times 10^{-10} \text{m}\); dotted curve: Debye–Hückel limiting law.

Figure 10.3 shows that with the proper choice of the parameter \(a\), the mean ionic activity coefficient of HCl calculated from Eq. 10.4.7 (dashed curve) agrees closely with experiment (solid curve) at low molalities.

As the molalities of all solutes become small, Eq. 10.4.7 becomes

\[
\ln \gamma_{\pm} = -A_{\text{DH}} \left| z_+z_- \right| \sqrt{I_m}\tag{10.4.8}
\]

This form is known as the **Debye–Hückel limiting law**. Note that the limiting law contains no adjustable parameters. The dotted curve in Fig. 10.3 shows that the limiting law agrees with experiment only at quite low molality.

The ionic strength \(I_m\) is calculated from Eq. 10.4.2 with the molalities of all ions in the solution, not just the molality of the ion or solute whose activity coefficient we are interested in. This is because, as explained above, the departure of \(\ln \gamma_{\pm}\) from the ideal-dilute value of \(\ln 1\) is caused by the interaction of each ion with the ion atmosphere resulting from all other ions in the solution.

In a binary solution of a single electrolyte solute, assumed to be completely dissociated, the relation between the ionic strength and the solute molality depends on \(\nu\) (the number of ions per solute formula unit) and the charge numbers \(z_+\) and \(z_-\). The ionic strength is given by

\[
I_m = (1/2)\sum_i m_i z_i^2 = (1/2)(\nu_+z_+^2+\nu_-z_-^2)m_B.
\]

With the help of the electroneutrality condition \(\nu_+z_+ = -(\nu_-z_-)\), this becomes

\[
I_m = \textstyle\frac{1}{2}\nu\left|z_+z_-\right|m_B\tag{10.4.9}
\]

We find the following relations hold between \(I_m\) and \(m_B\) in the binary solution, depending on the stoichiometry of the solute formula unit:

- For a 1:1 electrolyte, e.g., NaCl or HCl: \(I_m = m_B\)
- For a 1:2 or 2:1 electrolyte, e.g., Na\(_2\)SO\(_4\) or CaCl\(_2\): \(I_m = 3m_B\)
• For a 2:2 electrolyte, e.g., MgSO\(_4\): \(I_m = 4\text{mB}\)
• For a 1:3 or 3:1 electrolyte, e.g., AlCl\(_3\): \(I_m = 6\text{mB}\)
• For a 3:2 or 2:3 electrolyte, e.g., Al\(_2\)(SO\(_4\))\(_3\): \(I_m = 15\text{mB}\)

Figure 10.4 shows \(\ln g_{\pm}\) as a function of \(\sqrt{I_m}\) for aqueous HCl (upper curves) and aqueous CaCl\(_2\) (lower curves). The experimental curves have the limiting slopes predicted by the Debye–Hückel limiting law (Eq. 10.4.8), but at a low ionic strength the curves begin to deviate significantly from the linear relations predicted by that law. The full Debye–Hückel equation (Eq. 10.4.7) fits the experimental curves over a wider range of ionic strength.

Contributors

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