# Debye-Huckel Theory

Ionic atmosphere

Solutions of electrolytes are non-ideal at relatively low concentrations. The activities of ions in solution is relatively large compared to neutral compounds. Ions interact through a Coulombic potential that varies as $1/r$ (r is the distance between ions). Neutral solutes interact through London dispersion forces that vary as $1/r^6$. The greater the charge on the ions the larger the deviations from ideality. For example, per mole of $CaCl_2$ dissolved the deviation from ideal behavior is larger than for NaCl due to the 2+ charge of calcium ion. These considerations lead to the concept of an ionic atmosphere.

Ionic solutions

We consider a general salt $C_{\nu+}A_{\nu-}$, which dissociates into n_+ cations and n_- anions per formula unit

$$C_{\nu+}A_{\nu-} \,(s) \rightarrow \nu_+ C^{z+} \,(aq) + \; \nu_+ A^{z-} \,(aq)$$
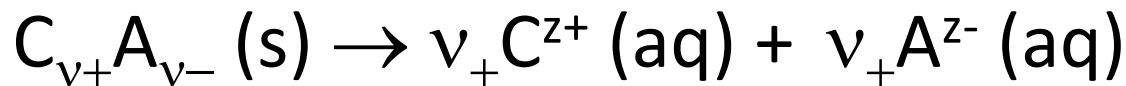
Where $\nu_+ z_+ + \nu_- z_- = 0$ by electroneutrality. We write the chemical potential of the salt in terms of the chemical potentials of its constituent ions according to

$$\mu_2 = \nu_+ \mu_+ + \nu_- \mu_-$$

where the subscript 2 refers to the ionic solute.

Ionic solutions

As for neutral solutes we have

$$\mu_2 = \mu_2^o + RT \ln a_2$$

but for ionic solutes we have that

$$\mu_+ = \mu_+^o + RT \ln a_+$$

and

$$\mu_- = \mu_-^o + RT \ln a_-.$$

$$\nu_+ \ln a_+ + \nu_- \ln a_- = \ln a_2$$

which implies that $a_2 = a_+^{n+} a_-^{n-}$

We can use this development of introduce the mean ionic activity.

$$a_\pm^n = a_+^{n+} a_-^{n-} \text{ where } \nu = \nu_+ + \nu_-.$$

Ionic solutions

We cannot define the activity coefficients of individual ions, but we can determine the mean activity coefficients by the same means used to determine the activity coefficients of other substances. The mean activity coefficients are defined based on single-ion activity coefficients

$a_+ = m_+\gamma_+$ and $a_- = m_-\gamma_-$

where m_+ and m_- are the molalities of the individual ions given by

$m_+ = \nu_+ m$ and $m_- = \nu_- m$.

Ionic solutions

In analogy with the definition of the mean ionic activity $a_\pm$ we define a mean ionic molality, $m_\pm$ by

$$m_\pm{}^n = m_+{}^{n+}\, m_-{}^{n-}$$

and a mean ionic activity coefficient, $g_\pm$ by

$$\gamma_\pm{}^n = \gamma_+{}^{n+}\, \gamma_-{}^{n-}.$$

Given these definitions we can write

$$a_\pm{}^n = m_\pm{}^n \gamma_\pm{}^n$$

Activity coefficient

At low concentrations of ionic solute the mean activity coefficient goes as

$$\ln \gamma_{\pm} = -\,1.173 |z_+ z_-| (I_c / c^o)^{1/2}$$

Here c_o is 1 mol/L and where z_+ and z_- are the charge of the positive and negative ions involved in a chemical reaction. This is the concentration in the standard state. This standard concentration cancels the units of ionic strength.

Ionic strength

The ionic strength is calculated using:

$$I_c = \frac{1}{2}\left(z_+^2 c_+ + z_-^2 c_- \right)$$

where z_+ and z_- are the charge of the positive and negative ions, respectively and c_+ and c_- are their concentrations. It is important to note that z_+ and z_- ions that make up the solution are not necessarily the same charge as those involved in the chemical reaction. In other words, excess ions in solution contribute to the ionic atmosphere.

Origin of the Debye-Huckel Theory

Where does the factor of 1.173 come from? In 1925 Debye and Huckel derived the following form for the activity coefficient in ionic solutions.

$$\ln \gamma_{\pm} = - \frac{\kappa q_j^2}{8\pi\varepsilon_0\varepsilon_r kT}$$

This expression is based on Coulomb's law and on the concept of a Debye length $1/\kappa$.

The concept of Debye length

This expression is based on Coulomb's law and on the concept of a Debye length $1/\kappa$. The Debye length can be thought of the approximate radius of the ionic atmosphere of an ion. For a 1-1 electrolyte

$$\frac{1}{\kappa} = \frac{304 \; pm}{\sqrt{c \; mol/L}}$$

When the concentration of the electrolyte is 0.01 M the Debye length is approximately 3000 pm or 3 nm.

Limitations of the Debye-Huckel approximation

The general formula for κ is:

$$\kappa = \sqrt{\frac{2e^2 N_A 1000(L/m^{-3})}{\varepsilon_0 \varepsilon_r kT} I_c / mol/L}$$

Debye-Hückel theory is valid only in the limit of low concentrations. The theory breaks down when the concentration of the electrolyte is greater than about 100 mM.