5.7: Electrolyte Solutions

An electrolyte solution is a solution that generally contains ions, atoms or molecules that have lost or gained electrons, and is electrically conductive. For this reason they are often called ionic solutions, however there are some cases where the electrolytes are not ions. For this discussion we will only consider solutions of ions. A basic principle of electrostatics is that opposite charges attract and like charges repel. It also takes a great deal of force to overcome this electrostatic attraction.

Introduction

The general form of Coulomb's law describes the force of attraction between charges:

$$F = k\frac{q_1 m q_2}{r^2} \tag{5.7.1}$$

However, we must make some changes to this physics formula to be able to use it for a solution of oppositely charged ions. In Coulomb's Law, the constant

$$k = \frac{1}{4\pi\varepsilon_0} \tag{5.7.2}$$

, where ε_0 is the permittivity of free space, such as in a vacuum. However, since we are looking at a solution, we must consider the effect that the medium (the solvent in this case) has on the electrostatic force, which is represented by the dielectric constant ε:

$$F = \frac{q_1 q_2}{4\pi\varepsilon_0 \varepsilon r^2} \tag{5.7.3}$$

Polar substances such as water have a relatively high dielectric constant.

Standard Definitions of Enthalpy, Entropy, and Gibbs Energy for Ions

Ions are not stable on their own, and thus no ions can ever be studied separately. Particularly in biology, all ions in a certain cell or tissue have a counterion that balances this charge. Therefore, we cannot measure the enthalpy or entropy of a single ion as we can atoms of a pure element. So we define a reference point. The $\Delta_f \overline{H}^\circ$ of a hydrogen ion H^+ is equal to zero, as are the other thermodynamic quantities.

$$\Delta_f \overline{H}^\circ [H^+(aq)] = 0 \tag{5.7.4}$$

$$\Delta_f \overline{G}^\circ [H^+(aq)] = 0 \tag{5.7.5}$$

$$\overline{S}^\circ [H^+(aq)] = 0 \tag{5.7.6}$$

When studying the formation of ionic solutions, the most useful quantity to describe is chemical potential μ, defined as the partial molar Gibbs energy of the ith component in a substance:

$$\mu_i = \overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i^\circ + RT\ln x_i \tag{5.7.7}$$

where x_i can be any unit of concentration of the component: mole fraction, molality, or for gases, the partial pressure divided by the pressure of pure component.

Ionic Solutions

To express the chemical potential of an electrolyte in solution in terms of molality, let us use the example of a dissolved salt such as magnesium chloride, $MgCl_2$.

$$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^- \tag{5.7.8}$$

We can now write a more general equation for a dissociated salt:

$$M_{\nu+}X_{\nu-} \rightleftharpoons \nu_+ M^{z+} + \nu_- X^{z-} \tag{5.7.9}$$

where $\nu_\pm$ represents the stoichiometric coefficient of the cation or anion and $z_\pm$ represents the charge, and M and X are the metal and halide, respectively.

The total chemical potential for these anion-cation pair would be the sum of their individual potentials multiplied by their stoichiometric coefficients:

$$\mu = \nu_+ \mu_+ + \nu_- \mu_- \tag{5.7.10}$$

The chemical potentials of the individual ions are:

$$\mu_+ = \mu_+^\circ + RT \ln m_+ \tag{5.7.11}$$

$$\mu_- = \mu_-^\circ + RT \ln m_- \tag{5.7.12}$$

And the molalities of the individual ions are related to the original molality of the salt m by their stoichiometric coefficients

$$m_+ = \nu_+ m \tag{5.7.13}$$

Substituting Equations 5.7.11 and 5.7.12 into Equation 5.7.10,

$$\mu = (\nu_+ \mu_+^\circ + \nu_- m u_-^\circ) + RT \ln\left(m_+^{\nu+} m_-^{\nu-}\right) \tag{5.7.14}$$

since the total number of moles $\nu = \nu_+ + \nu_-$, we can define the mean ionic molality as the geometric average of the molarity of the two ions:

$$m_\pm = \left(m_+^{\nu+} m_-^{\nu-}\right)^{\frac{1}{\nu}} \tag{5.7.15}$$

then Equation 5.7.14 becomes

$$\mu = (\nu_+ \mu_+^\circ + \nu_- \mu_-^\circ) + \nu RT \ln m_\pm \tag{5.7.16}$$

We have derived this equation for a ideal solution, but ions in solution exert electrostatic forces on one another to deviate from ideal behavior, so instead of molarities we must use the activity a to represent how the ion is behaving in solution. Therefore the mean ionic activity is defined as

$$a_\pm = \left(a_+^{\nu+} + a_-^{\nu-}\right)^{\frac{1}{\nu}} \tag{5.7.17}$$

where

$$a_\pm = \gamma m_\pm \tag{5.7.18}$$

and $\gamma_\pm$ is the **mean ionic activity coefficient**, which is dependent on the substance.

Substituting the mean ionic activity of \Equation 5.7.18 into Equation 5.7.16,

$$\mu = (\nu_+ \mu_+^\circ + \nu_- \mu_-^\circ) + \nu RT \ln a_\pm = (\nu_+ \mu_+^\circ + \nu_- \mu_-^\circ) + RT \ln a_\pm^\nu = (\nu_+ \mu_+^\circ + \nu_- \mu_-^\circ) + RT \ln a \tag{5.7.19}$$

when $a = a_\pm^\nu$. Equation 5.7.19 then represents the chemical potential of a nonideal electrolyte solutions. To calculate the mean ionic activity coefficient requires the use of the Debye-Hückel limiting law, part of the Debye-Hückel theory of electrolytes .

✔ **Example 5.7.1**

Let us now write out the chemical potential in terms of molality of the salt in our first example, $MgCl_2$. First from Equation 5.7.8, the stoichiometric coefficients of the ions are:

$$\nu_+ = 1, \nu_- = 2, \nu = 3$$

The mean ionic molality is

$$m_\pm = \left(m_+^1 m_-^2\right)^{\frac{1}{3}}$$

$$= (\nu_+ m \times \nu_- m)^{\frac{1}{3}}$$

$$= m(1^1 2^2)^{\frac{1}{3}}$$

$$= 1.6\, m$$

The expression for the chemical potential of

$$MgCl_2 \tag{5.7.20}$$

is

$$\mu_{MgCl_2} = \mu^{\circ}_{MgCl_2} + 3RT \ln 1.6 \backslash mm$$

References

1. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, California: University Science Books, 2005.

Contributors and Attributions

- Konstantin Malley

5.7: Electrolyte Solutions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.