

5.9: Colligative Properties of 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:

$$[Math Processing Error]$$

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 $[Math Processing Error]$, where $[Math Processing Error]$ 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 $[Math Processing Error]$:

$$[Math Processing Error]$$

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 $[Math Processing Error]$ of a hydrogen ion $[Math Processing Error]$ is equal to zero, as are the other thermodynamic quantities.

$$[Math Processing Error]$$

$$[Math Processing Error]$$

$$[Math Processing Error]$$

When studying the formation of ionic solutions, the most useful quantity to describe is chemical potential $[Math Processing Error]$, defined as the partial molar Gibbs energy of the i th component in a substance:

$$[Math Processing Error]$$

where $[Math Processing Error]$ 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, $[Math Processing Error]$.

$$[Math Processing Error]$$

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

$$[Math Processing Error]$$

where $[Math Processing Error]$ represents the stoichiometric coefficient of the cation or anion and $[Math Processing Error]$ 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:

$$[Math Processing Error]$$

The chemical potentials of the individual ions are:

$$[Math Processing Error]$$

$$[Math Processing Error]$$

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

$$[Math Processing Error]$$

Substituting Equations $[Math Processing Error]$ and $[Math Processing Error]$ into Equation $[Math Processing Error]$,

$$[Math Processing Error]$$

since the total number of moles $[Math Processing Error]$, we can define the mean ionic molality as the geometric average of the molality of the two ions:

$$[Math Processing Error]$$

then Equation $[Math Processing Error]$ becomes

$$[Math Processing Error]$$

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 molalities we must use the activity a to represent how the ion is behaving in solution. Therefore the mean ionic activity is defined as

$$[Math Processing Error]$$

where

$$[Math Processing Error]$$

and $[Math Processing Error]$ is the **mean ionic activity coefficient**, which is dependent on the substance.

Substituting the mean ionic activity of Equation $[Math Processing Error]$ into Equation $[Math Processing Error]$,

$$[Math Processing Error]$$

when $[Math Processing Error]$. Equation $[Math Processing Error]$ 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 $[Math Processing Error]$

Let us now write out the chemical potential in terms of molality of the salt in our first example, $[Math Processing Error]$. First from Equation $[Math Processing Error]$, the stoichiometric coefficients of the ions are:

$$[Math Processing Error]$$

The mean ionic molality is

$$[Math Processing Error]$$

The expression for the chemical potential of $[Math Processing Error]$ is

$$[Math Processing Error]$$

References

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

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