

16.16: Electrolytic Solutions

Thus far in our discussion of solute activities, we have assumed that the solute is a molecular species whose chemical structure is unchanged when the pure substance dissolves. This is not the case when salts dissolve in water and other polar solvents. A pure solid salt exists as a lattice of charged ions, rather than electrically neutral molecular moieties, and its solutions contain solvated ions. Since salt solutions conduct electricity, we often call them **electrolytic solutions**. Solutions of salts in water are extremely important from both practical and theoretical standpoints. Accordingly, we focus our discussion on aqueous solutions; however, the ideas that we develop apply to salt solutions in any solvent that supports the formation of solvated ions.

We can apply the concepts that we develop in this chapter to measure the activities of aqueous salt solutions. When we do so, we find new features. These features arise from the formation of aquated ionic species and from electrical interactions among these species. In this chapter, we consider only the most basic issues that arise when we investigate the activities of dissolved salts. We consider only **strong electrolytes**; that is, salts that are completely dissociated in solution. In this section, we briefly review the qualitative features of such solutions.

Departure from Henry's law behavior begins at markedly lower concentrations when the solute is a salt than when it is a neutral molecular species. This general observation is easily explained: Departures from Henry's law are caused by interactions among solution species. For neutral molecules separated by a distance r , the variation of the interaction energy with distance is approximately proportional to r^{-6} . This means that only the very closest molecules interact strongly with one another. For ions, Coulomb's law forces give rise to interaction energies that vary as r^{-1} . Compared to neutral molecules, ions interact with one another at much greater distances, so that departures from Henry's law occur at much lower concentrations.

Our qualitative picture of an aqueous salt solution is that the cations and anions that comprise the solid salt are separated from one another in the solution. Both the cations and the anions are surrounded by layers of loosely bound water molecules. The binding results from the electrical interaction between the ions and the water-molecule dipole. The negative (oxygen) end of the water dipole is preferentially oriented toward cations and the positive (hydrogen) end is preferentially oriented toward anions.

In aqueous solution, simple metallic cations are coordinated to a first layer of water molecules that occupy well-defined positions around the cation. In this layer, the bonding can have a covalent component. Such combinations of metal and coordinated water molecules are called **aquo complexes**. For most purposes, we can consider that the aquo complex is the cationic species in solution. Beyond the layer of coordinated water molecules, a second layer of water molecules is less tightly bound. The positions occupied by these molecules are more variable. At still greater distances, water molecules interact progressively more weakly with the central cation. In general, when we consider the water molecules that surround a given anion, we find that even the closest solvent molecules do not occupy well-defined positions.

In any macroscopic quantity of solution, each ion has a specific average concentration. On a microscopic level, the Coulomb's law forces between dissolved ions operate to make the relative locations of cations and anions less random. It is useful to think about a spherical volume that surrounds a given ion. We suppose that the diameter of this sphere is several tens of nanometers. Within such a sphere centered on a particular cation, the concentration of anions will be greater than the average concentration of anions; the concentration of cations will be less than the average concentration of cations. Likewise, within a microscopic sphere centered on a given anion, the concentration of cations will be greater than the average concentration of cations; the concentration of anions will be below average.

As the concentration of a dissolved salt increases, distinguishable species can be formed in which a cation and an anion are nearest neighbors. We call such species **ion pairs**. At sufficiently high salt concentrations, a significant fraction of the ions can be found in such **ion-pair complexes**. Compared to other kinds of chemical bonds, ion-pair bonds are weak. The ion-pair bond is labile; the lifetime of a given ion pair is short. At still higher salt concentrations, the formation of significant concentrations of higher aggregates becomes possible. Characterizing the species present in an electrolytic solution becomes progressively more difficult as the salt concentration increases.

This page titled [16.16: Electrolytic Solutions](#) 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.