CLASSICS

At the time of Ostwald, the properties of solutions were extensively studied. Often, the observed osmotic pressures were considerably higher than that expected based upon the number of molecules that were in the solution. Further, the solutions were found to be conductors of electricity. These were explained by the Arrhenius theory of electrolytic dissociation, viz., in general, salts in solution dissociate to give ions. Ostwald, in 1888 gave a quantitative description of the dissociation, which was very useful in understanding the physical chemistry of solutions. The following portion 'The Ions' is from the book *The Fundamental Principles of Chemistry*, written by him.

K L Sebastian

The Ions
by Wilhelm Ostwald

208. Electrolytic Dissociation. – The transformation of a salt into its ions within a solution is called *electrolytic dissociation*, and this process is a chemical reaction coming under the general laws already discussed. A salt solution gives back the original salt unchanged when it is evaporated, and this proves clearly that the dissociation into ions is reversed when the salt separates. The question arises whether dissociation is complete within the solution or not. In other words, does a quantitative equilibrium exist between the unchanged salt and its ions?

The answer is in the affirmative. It is precisely because such a finite equilibrium usually exists that the simple relations of Sec. 206 must be confined to very dilute solutions. When a salt breaks up into its ions, a corresponding increase in osmotic pressure accompanies the increase in the molar concentration of the solution, and if the osmotic pressure is forcibly changed by dilution or concentration, reactions will be set up which resist the change. If concentration takes place and the osmotic pressure is forcibly increased, that reaction will take place which tends to diminish the pressure, and if dilution is brought about the reaction will take place which increases the pressure. The first of these reactions consists in the formation of undissociated salt, the second reaction

in more complete dissociation. Concentration of a salt solution therefore leads finally to the separation of the salt in the solid, undissociated form, while dilution leads finally to a complete dissociation into ions. Between these two limits eqlibrium corresponding to the general law of mass action will exist.

In the simplest case in which two univalent ions make up a salt, this may be expressed as follows: K is the cation, A the anion, S the salt, and equation for the reaction will be $K + A = S$. If k, a, and s are the concentrations of these substances the equilibrium equation is $\dfrac{a \cdot k}{s} = C$. The equation is based on one mol of the salt, and we will let x be the fraction of this mol which is broken up into ions; then $1 - x$ would be the unchanged portion, and we will use v for the total volume. The concentrations are then $a = \dfrac{x}{v}$, $k = \dfrac{x}{v}$, and $s = \dfrac{(1-x)}{v}$. Substituting these in the equilibrium equation, we have $\dfrac{x^2}{(1-x)\,v} = C$.

This equation was first suggested by Ostwald in 1888, and it represents the general behaviour of electrolytes in a qualitative way. In regions of small and medium dissociation it has quantitative accuracy. In the limiting case of more complete dissociation deviations occur which have not yet been fully cleared up. If v is very large, which is the case for unlimited dilution, x approaches unity and $1-x$ approaches zero; that is, the dissociation is complete. The constant C has an individual value for each electrolyte or salt, and it frequently shows relations to composition and constitution.

In cases where a larger number of different ions are present in a solution the law of mass action is still applicable, and a large number of various phenomena characteristic of ions may be represented by its use. This application does not, however, lead to anything new or of fundamental importance, and the simple example given is therefore sufficient to make the existing relations clear.