Review of the Theory of Electrolytic Conductance¹

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The Ostwald dilution law, based on the Arrhenius hypothesis of electrolytic dissociation, was the first theoretical formulation of the dependence of conductance on concentration. While it adequately described the conductance of weak electrolytes, it could not account for the observation by Kohlrausch that, at low concentrations, the equivalent conductance $\Lambda$ of strong electrolytes approached linearity in $c^{1/2}$, the square root of concentration. Debye and Hückel (1923) assumed complete dissociation and calculated the theoretical behavior of rigid charged spheres moving in a continuum (the primitive model); the result was prediction of the Kohlrausch result. Onsager (1927) predicted the exact numerical value of the limiting slope for the $\Lambda$ vs. $c^{1/2}$ curves. Bjerrum (1926) suggested association of ions to pairs which would not contribute to the long-range interionic effects considered by Debye and Hückel. Fuoss and Kraus (1933) corrected the Ostwald dilution law for the DHO square-root terms and obtained a $\Lambda(c)$ function which satisfactorily accounted for conductance curves which lay below the limiting tangent. Investigations of the effects of higher terms which had been neglected in the classical DHO treatment of the primitive model led to $\Lambda(c)$ functions which lay above the limiting tangent for completely dissociated electrolytes. By combining these higher-term equations with Bjerrum pairing, a generally useful conductance function was obtained (Fuoss–Hsia, 1957). In order to eliminate a number of inconsistencies between the properties of real systems and those of the primitive model, a new model (Fuoss, 1975) was proposed: ion pairs are defined as those whose center-to-center distance lies in the range $a \leq r \leq R$, where $R$ is the diameter of the Gurney cosphere. Later (1977) the paired ions were divided into two categories: ions which have only solvent molecules as nearest neighbors, and ions which have one ion of opposite charge as a member of the inner shell. The latter contribute only to charging current.

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Experimental observations have shown that electrolytic conductance depends on the thermodynamic variables concentration, temperature, and pressure, on dielectric constant and viscosity of solvent, on valence type of the electrolyte, on field strength and frequency used in measurement, and on variously defined parameters which describe short range ion–ion and ion–solvent interactions. For a given system at fixed temperature and pressure, measured at low field strength and low frequency, the theoretical problem reduces to prediction of the concentration dependence of conductance. The specific conductance $\sigma$ (corrected for solvent conductance) approaches zero as concentration decreases to zero in such a way that $\lim (\sigma/c)$ approaches a constant. Equivalent conductance $\Lambda(c)$ is defined as $1000 \sigma/c$; limiting conductance $\Lambda_0$ is the limit of $\Lambda(c)$ at $c = 0$. A preliminary statement of the problem might be: Given the experimental observation that $\Lambda = \Lambda_0 - F_{\text{obs}}(c)$ where $F_{\text{obs}}(0) = 0$, derive a function $F_{\text{th}}(c)$ such that, for a set of data points $(c_k, \Lambda_k)$, $[\Lambda_0 - F_{\text{th}}(c_k)]$ will equal the observed $\Lambda_k$'s within the estimated experimental error. Obviously an infinite set of such functions exists: $F_{\text{th}} = F(c; C_1, \ldots, C_m)$, where the constants $C_j$ depend on the functional form chosen for $F$. This arithmetic approach is, of course, without value; the informative goal is a function $F_{\text{th}} = F(c; P_1, \ldots, P_m)$ where the $P_j$'s are parameters which have physical significance in the sense that they can be correlated with properties of solute and solvent. The basic problem therefore is not mathematical but physical: Construct a model, the properties of which correspond as closely as feasible to those of real systems, and then derive its conductimetric behavior by the standard methods of mathematical physics. The historical development of the theory of conductance parallels successive improvements in the models used.

The first model was thermodynamic: Arrhenius postulated an equilibrium

$$\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^- \quad (1)$$

between neutral molecules AB and the free ions A$^+$ and B$^-$ into which AB dissociates, the fraction $\gamma$ of free ions being measured by the conductance ratio $\Lambda/\Lambda_0$. The mass-action equation of Guldberg and Waage

$$[\text{A}^+] [\text{B}^-]/[\text{AB}] = c\gamma^2/(1 - \gamma) = K_{\text{diss}} \quad (2)$$

then leads to the Ostwald dilution law

$$c\Lambda^2 = K_{\text{diss}} \Lambda_0^2 (1 - \Lambda/\Lambda_0) \quad (3)$$

A paradox was discovered quite early: For aqueous solutions of weak acids and bases, the dissociation constants calculated by (3) from $(c_k, \Lambda_k)$ data proved to be practically constant, but for solutions of strong acids and bases