

Vapour Phase Electrochemistry 1. The Missing Science.

Appendix B. Limitations of the Debye-Hückel Model.

The basic Debye-Hückel model (Debye and Hückel, 1923) has been used as a fundamental element in treating the properties of electrolyte solutions for nearly a century. It is applied to both equilibrium properties and to rate processes such as conductance. The theory attempts to derive the radial distribution function for ions of one charge around a single ion of the opposite charge by combining Boltzmann's energy distribution law with Coulomb's law of electrostatic attraction. Essentially, the energy difference between an originally charge-free fluid and an appropriately charged one is calculated.

Consequently, it involves an exponential function that is the ratio of the electrostatic energy of the system to its thermal energy. It has long been realized that there are serious problems with many of the approximations needed in its development - but it is still the only simple model that has proved to be of much practical use. One obvious limitation is that the model ignores the molecular structure of a solution. As pointed out by MacInnes (1961) on pg 148, "There is no detail of the derivation of the equations of the Debye-Hückel theory that has not been criticized".

The problem discussed most frequently arises from the mathematical expansion of an exponential function (involving ratios of the electrostatic and thermal forms of energy) to a power series and retaining only the first term in the expansion. Numerous experiments have shown that the predictions of the model are very reliable at very low concentrations and that this tends to be true even for solutions far more concentrated than those for which the theory should break down (see e.g. Harned and Owen, 1950; Robinson and Stokes, 1955). It seems that more elaborate theories must have all tended to provide *worse fits to experimental data than the simple version*.

Before the Debye-Hückel model had been developed, a wide variety of different approaches had been proposed which attempted to address the problems of quantifying the consequences of a far earlier discovery. This was by Arrhenius (1887) and it showed that, when sufficiently dilute, solutions of electrolytes are always fully dissociated into ions. Some electrolytes are fully dissociated into ions at *any* concentration while others only become fully dissociated in very dilute solutions. These chemical species are described respectively as strong and weak electrolytes. The degree of dissociation is normally only of *practical* importance when *acids* could be involved since their degrees of dissociation control the pH of any mixture.

One of the less frequently considered problems with the Debye-Hückel theory is that neither of the two energy terms it employs allows for a change in volume. In other words, the mechanical work done during the charging process is ignored. Hence, in a compressible electrolyte solution, neither the thermodynamic nor the kinetic properties can possibly be *validly* calculated and there *should be* no expectation that the theory is valid under these conditions. The evidence of Fig. 1 confirms that the theory is completely useless when a solution is sufficiently compressible.

In recent years, many studies of the solution chemistry of electrolytes have abandoned the hope of trying to use analytic expressions in favour of using either molecular dynamics simulations or Monte-Carlo approximations (see e.g. Franks, 1973). However, despite its well known limitations, the Debye-Hückel model is still used in interpreting most experimental results. As seen in Section 2.1, even solutions at 25^o C are actually somewhat compressible. One obvious improvement to the Debye-Hückel model would have been to add an energy term involving the compressibility of the solvent. This obvious suggestion would have been tried early on but, it seems, its neglect allowed the simpler theory to be applied to significantly more concentrated solutions.

Appendix B. References:

Arrhenius, S. (1887). Über die Dissociation der in Wasser gelösten Stoffe" Zeit. Phys Chemie. 1, 631-648. <https://doi.org/10.1515/zpch-1887-0164>.

Debye, P. and Hückel, E. (1923). Zur Theorie der Elektrolyte.1. Gefrierpunktserniedrigung und verwandte Erscheinungen. Physik. Zeit. 24. 185-206.

Franks, F. (1973). Water: A Comprehensive Treatise. Vol 3.Aqueous Solutions of Simple Electrolytes. Plenum Press, London.

Harned, H.S. and Owen, B.B. (1950). The Physical Chemistry of Electrolytic Solutions. Reinhold Publishing Co., New York, NY.

MacInnes, D.A. (1961). The Principles of Electrochemistry. Dover Publications Inc. New York, NY.

Robinson, R.A. and Stokes, R.H. (1955). Electrolyte Solutions, Butterworths Sci. Publ., London.