Solution Chemistry Simplified Based on Arrhenius' Theory of Electrolytic Dissociation and Hydration For all Concentrations

- Collected research work, dedicated to Svante August Arrhenius (1859 – 1927).

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Abstract: Arrhenius theory of partial dissociation of electrolytes rose to its heights and fame when he was awarded the Nobel Prize (1903). While the theory was still being developed to account for the non-ideal properties of electrolytes at higher concentrations, it was unfortunately replaced by Lewis' empirical concepts of activity and activity coefficients. With the near success of the Debye-Huckel theory of inter-ionic interactions for very dilutions, the latter was erroneously extended over the next few decades by extended parametrical equations to higher concentrations assuming complete dissociation at all concentrations. This eventually turned solution theory into a mere catalogue of parameters. Therefore, the present author abandoned it all and started systematically analyzing the available experimental data as such. She found that with the degrees of dissociation and 'surface' and 'bulk' hydration numbers obtained from vapour pressure data, properties of electrolytes could be explained quantitatively over the whole concentration range, using simple mathematical equations.

Keywords. Arrhenius; Partial dissociation; Hydration; Surface and bulk hydration numbers; Strong electrolytes; Solution thermodynamics.

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1. Introduction.

Over a century ago, Svante Arrhenius laid the foundations for the theory of electrolytic dissociation [1]. Initially it met with mistrust [2], but the theory soon gained confirmation and confidence and he was awarded the Nobel Prize in 1903. According to his original theory [1], a fraction **(α)** mole of an electrolyte like NaCl dissociates in water into 2α moles of ions, the rest (1-α) being in the undissociated form:

$$\mathbf{NaCl\ (1\text{-}\alpha) \leftrightarrow Na^{+}(\alpha) + Cl^{-}(\alpha)} \qquad \mathbf{(1)}$$

Thus every mole of salt, on dissolving in water, increased to $(1\text{-}\alpha) + 2\alpha = (1+\alpha) = i\ (> 1)$, where i is the van't Hoff factor. The Arrhenius conductivity ratio, taken as the ratio of the equivalent conductivity at any concentration (Λ) to that at infinite dilution (Λ_o) as a measure of the degree of dissociation (α), explained the van't Hoff factor as the increase in osmotic pressure. This theory was greatly successful in explaining many other properties of dilute electrolyte solutions. Arrhenius and his supporters, van’t Hoff and Ostwald became known as the ‘Ionists’ [2,3].

While modifications of the conductivity ratio were being tried to extend the theory to concentrated solutions, and allowance for hydration and the idea of ‘free water’ were being developed [4], Lewis and Randall [5] replaced the use of ‘true ionic concentrations’ in solution thermodynamics by their empirical concepts of activity and activity coefficient correction factors. This was protested by many including by Bancroft, the then Editor of the Journal of Physical Chemistry [3].

Since the Debye-Huckel [6] theory of interionic interaction for complete dissociation of electrolytes, as shown,

$$\mathbf{NaCl \rightarrow Na^{+} + Cl^{-}} \qquad \textbf{(2)}$$

was able to nearly explain the concentration dependence of activity coefficients for very dilute solutions, the latter equations based on complete dissociation were gradually extended to higher concentrations until they resulted in extremely elaborate equations with many unknown parameters (see e.g., [7,8]) without any physical significance. Moreover, there was no unified explanation of non-ideality over the whole concentration range.This clearly indicated [9,10] that there was some basic flaw in the underlying theory of electrolytes.

2. Present solution theory based on partial dissociation and hydration [12-73]

The author became aware of the complexity of the theory of solutions of simple alkali halides like NaCl (aq) during her doctoral work [11] on aqueous solutions of strong electrolytes. In the following post-doctoral years, she abandoned the existing theory and started reinvestigating the available experimental data on the properties of electrolytes [12,13]. Gradually it became clear that, with the degrees of dissociation (α) and the hydration numbers evaluated from the vapour pressure (or osmotic coefficient) data (instead of from the conductivity ratio), the original idea of partial dissociation due to Arrhenius, as per equation (1), and of 'free water' [4], could explain quantitatively the non-ideal properties of electrolytes over a large range of concentrations [12- 40].

Further advance was made in 1995 [41-44] by the author, when she found that the hydration numbers and hence the molalities of free water in the "surface and bulk of solution" are different. This made it possible to extend the theory of electrolytes based on the idea of partial dissociation and free water to the whole range of concentrations from "zero to saturation". The full paper was accepted (after refusal by a few other journals) with praise twenty years ago in JES [44]). Many thermodynamic properties of solutions could thus be explained quantitatively in terms of simple mathematical relations involving the degrees of dissociation, hydration numbers and volumes of ions and ion pairs. For review papers on the subject, see [49,50], [64], [67], [71] and [72]. A summarizing Table of simple equations describing the thermodynamic properties of aqueous electrolytes can be found in [72]

This work was appreciated by the award of the Invitation Plenary Lecturership to the author for the "Svante Arrhenius Symposium" in Sweden in 2003 commemorating the centenary of the award of the Nobel Prize to Arrhenius in 1903. See for the full text of the talk, [64] and [67],where Tables of data for many electrolytes can be found.

Refs. [1- 10] in Part I pertain to the Introduction and [11-39] in Part II & [40-73] in Part III pertain to the author’s work on electrolytes in aqueous solutions from 0 to ~3m and “from 0 to saturation” respectively. In [36], the anomalous Stokes ionic radii are explained. In [48,53,55], Bjerrum’s theory of ionic association was used in reverse to calculate the mean distance of approach of ions. Simple “equation-of-state” for all concentrations was established for gases [63] and for solutions [66].

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