Ask the Historian

The Proper Writing of Ionic Charges

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Question

Why in writing ionic charges do the charge signs follow rather than precede the numbers?

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Answer

Though the term "ion" was first introduced by Michael Faraday in 1834 (1), the concept of free ions in solution, and the corresponding need for a modification of conventional chemical symbolism in order to distinguish them from free atoms, did not come about until the introduction of Svante Arrhenius' theory of ionic dissociation in the 1880s (2). The impact of Arrhenius' theory on the introductory textbook was largely driven by the concomitant rise of modern physical chemistry in the 1890s under the leadership of the German chemist, Wilhelm Ostwald.

In his own textbooks Ostwald chose to represent the charge on positive ions by a series of superscripted dots placed to the right of the atomic symbol, and the charge on negative ions by a series of superscripted primes (3). Thus the barium cation was symbolized as $Ba^{\cdot\cdot}$ and the phosphate anion as PO_4'''. In contrast, the German chemist, Walther Nernst, in his equally influential 1893 textbook of theoretical chemistry, chose to place an appropriate number of superscripted + or - signs directly above the ion's atomic symbol (4), a practice which was soon modified by placing them instead to the immediate right of the symbol, as in Ba^{++} and PO_4^{---}(5).

The IUPAC guide to *Quantities, Units and Symbols* claims that yet a third "algebraic" method of indicating ionic charges was also used in the past in which the charge preceded the numerical value, as in Ba^{+2} and PO_4^{-3}, even though this particular sequence of symbols was originally intended to represent the inherent sign of a number or exponent and not the number of signs (6). However, inspection of nearly three dozen general, inorganic, and analytical textbooks, spanning the period 1909-1975, revealed that the vast majority employed the modified Nernst notation, with a smaller number – mostly of European or Russian origin – using the Ostwald notation instead. Rather surprisingly, very few examples of texts using the algebraic notation could be found, all of them post-1970 (7).

Figure 1. Svante Arrhenius (1859-1927).

Since at least the 1950s IUPAC has ruled that ionic charges or "charge numbers," as they are now officially called, should be written instead with the number preceding the charge sign, as in Ba^{2+} and PO_4^{3-} (6, 8, 9). There are several reasons for this decision. It is more concise than the typographically inelegant Nernst approach and more physically meaningful than the Ostwald notation. Unlike the algebraic notation, it avoids confusion with the conventional symbolism for inherently positive and negative numbers and maintains consistency in how we count physical entities. Thus, in counting apples, we say two apples, three apples, etc., not apples two, apples three – that is, the number always precedes the name of the entity be-

ing counted. Likewise, when counting charges, we should say two positive charges or three negative charges, not positive charges two or negative charges three. The IUPAC ruling was intended to make the charge number symbolism consistent with this verbal convention.

Most introductory chemistry textbooks now employ the IUPAC notation for ionic charges. However, while our survey of older textbooks uncovered only a few examples in which algebraic notation was used to symbolize ionic charges, it did disclose that this notation was used from a fairly early date to indicate so-called polar valence values or oxidation numbers (10) – a practice that is still widely found in general chemistry texts despite the fact that it is at variance with IUPAC recommendations, which unambiguously state that oxidation numbers are always to be symbolized using Roman numerals rather than Arabic numerals (6, 9).

Further confusion results from the fact that these same textbooks employ the algebraic notation to symbolize oxidation numbers when balancing redox equations, but the IUPAC Roman numeral notation when naming compounds using the Stock oxidation-number system. This eclecticism is further compounded by the fact that virtually all introductory texts also incorrectly state that the Stock system is to be used only when naming so-called ionic metal-nonmetal compounds (e.g iron(II) chloride for $FeCl_2$), whereas the stoichiometric prefix system is to be used only when naming so-called covalent nonmetal-nonmetal compounds (e.g. dinitrogen trioxide for N_2O_3). As even a superficial glance at the IUPAC rules shows, this is incorrect (9). Rather the Stock and prefix systems represent two alternative, but equally valid, naming systems applicable to all binary inorganic compounds irrespective of any imagined differences in their ionicity or covalency (11).

Literature Cited

1. M. Faraday, Faraday, *Experimental Researches in Electricity,* Vol. 1, Quaritch: London, 1839, p. 198.

2. Arrhenius' theory of ionic dissociation was first presented in his Ph.D. thesis of 1884, but did not attract widespread attention until the publication of the paper S. Arrhenius, "Über die Dissociation der in Wasser gelösten Stoffe," *Z. physik. Chem.*, **1887**, *1*, 631-648. An English translation is available in H. C. Jones, Ed., *The Modern Theory of Solution*, Harpers: New York, NY, 1899, pp. 47-67.

3. W. Ostwald, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, Engelmann: Leipzig, 1894.

4. W. Nernst, *Theoretische Chemie vom Standpunkte der Avogadroschen Regel und der Thermodynamik*, Enke: Stuttgart, 1893.

5. For a typical example, see H. P. Talbot, A. A. Blanchard, *The Electrolytic Dissociation Theory with Some of Its Applications,* Macmillan: New York, NY, 1907, p. 17.

6. E. R. Cohen et al., Eds, *Quantities, Units, and Symbols in Physical Chemistry*, 3rd ed., IUPAC and RSC Publishing: Cambridge, 2007, pp. 49-51.

7. For a typical example, see G. C. Pimentel, R. D. Spratley, *Understanding Chemistry*, Holden-Day: San Francisco, CA, 1971.

8. IUPAC, *Nomenclature of Inorganic Chemistry*, Butterworths: London, 1959, p. 26-32.

9. N. G. Connelly, et al., Eds., *Nomenclature of Inorganic Chemistry, IUPAC Recommendations 2005*, RSC Publishing: Cambridge, 2005, pp. 25-26, 31, 34, 47, 57, 65, 69, 76-80.

10. W. B. Jensen, "The Origin of the Oxidation-State Concept," *J. Chem. Educ.*, **2007**, *84*, 1418-1419.

11. W. B. Jensen, "Inorganic Myths in the Freshman Textbook," Invited lecture, 240th National ACS Meeting, Boston, MA, 26 August 2010. Copies available from author.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

Update

After publishing this article, it occurred to me that our generalized procedure for symbolizing nuclear charges in quantum mechanics as *Ze,* rather than as *eZ,* where *Z* is the number of charges (from the German *Zahl*) and *e* is the numerical value of an elementary charge, has a certain parallel with the arguments used here for the proper writing of ionic charges.