

The Origin of the Ionic-Radius Ratio Rules

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Question

What is the origin of the ionic radius ratio rules?

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Answer

Generally speaking, the ionic-radius ratio rules are either incorrectly attributed to Linus Pauling in the chemical literature (1) or to Victor Goldschmidt in the geochemical literature (2). In actual fact they were first proposed within the context of the coordination chemistry literature by the Austrian chemist, Gustav F. Hüttig (figure 1), in a brief note published in 1920 in which he reported the R/R_+ ratio for possible geometries corresponding to coordination numbers of 2, 3, 4, 5, 6, 8, 12 and 20 (3). Two years later the German chemist, Alfred Magnus, gave a more detailed treatment explicitly linked to Walther Kossel's recently proposed electrostatic screening theory of complex ion formation and also included values for various alternative coordination geometries, such as square-planar versus tetrahedral and hexagonal-planar versus octahedral (4, 5). In 1923 Hüttig's original results were cited by Max Lambert in a discussion of the structures of complex hydrates (6) and the following year they were incorporated into the second edition of Rudolf Weiland's textbook *Einführung in die Chemie der Komplexverbindungen* (7). In a series of papers published in 1925 by Rudolf Straubel and Hüttig, the rules were further linked to the concept of packing efficiency (8, 9).

The thrust of all of the above papers was the problem of how to predict the maximum coordination numbers for discrete complex ions and of explaining why there were few, if any, known examples of species having coordination numbers of five or seven. While not the first person to propose the radius ratio rules, the Swiss-Norwegian geochemist, Victor Goldschmidt, does appear to have been the first to apply them to infinitely extended ionic lattices rather than to discrete



Figure 1. Gustav Franz Hüttig (1890-1957).

complex ions – an application first described in German in 1926 and 1927 in Parts VII and VIII of his famous series of short monographs dealing with the laws governing the geochemical distribution of the elements in Nature and again in English in 1929 (10-12). Even this cannot be said of Pauling, however, who was quite late in coming to the rules and who first invoked them in his 1927 paper on ionic radii and once again in his 1929 summary of the various principles governing the structures of complex ionic crystals (13, 14).

In his various monographs Goldschmidt acknowledged the earlier work of both Hüttig and Magnus, whereas in his own publications Pauling failed to note either – an oversight which he partially corrected in the

case of Magnus a decade later in the first edition of *The Nature of the Chemical Bond* (15). This neglect, coupled with the unfamiliarity of most American chemists with both the early German literature on coordination chemistry and the geochemical literature probably accounts for the incorrect association of the rules with Pauling's name. Luckily this association has never been strong enough to become a full-fledged example of "Stigler's Law of Eponymy" (16):

No scientific discovery is ever named after its original discoverer.

though it is certainly an example of Robert Merton's more famous "Matthew Effect" (17) whereby the famous are often credited, not only with their own discoveries, but occasionally with some they never made:

For unto every one that hath shall be given, and he shall have abundance: but from him that hath not shall be taken away even that which he hath. (The Gospel of Saint Matthew)

While the ionic-radius ratio rules are known to have many exceptions, they have remained a standard feature of most inorganic textbooks since the 1950s and have also been the subject of numerous articles in this journal (18).

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