

# The Origin of the Term “Hypervalent”

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## Question

What is the origin of the term “hypervalent”?

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## Answer

The term *hypervalent* was first introduced by Jeremy Musher in 1969 to describe compounds and complex ions of the heavier main-block elements (period 3 and beyond) in which the use of traditional Lewis 2c-2e covalent bonds requires the additional assumption of “octet expansion” for the central atom (e.g.  $\text{PCl}_5$ ,  $\text{SiF}_6^{2-}$  etc.) (1). The debate over how to rationalize the bonding in these species goes back to the very origins of the electronic theory of the covalent bond and ultimately revolves around the question of whether the 2c-2e bond or the octet rule is the more rigorous bonding principle. In the 1920s a vigorous debate over this issue was carried on between G. N. Lewis and Irving Langmuir, with the former opting for octet expansion and the dominance of the 2c-2e bond (2) and the latter for the dominance of the octet rule, thus requiring the assumption that the bonding in hypervalent species was ionic rather than covalent (3).

In the late 1920s and early 1930s, Samuel Sugden, on the basis of parachor measurements, argued for the existence of 2c-1e covalent bonds and showed how they could be used, in conjunction with traditional 2c-2e covalent bonds, to rationalize the bonding in hypervalent species without the necessity of either violating the octet rule or invoking ionic bonding, but his suggestions were not widely accepted (4). Ironically, in the 1940s and 1950s essentially the same concept was invoked by Robert Rundle (figure 1) (5) and George Pimentel (6) via MO theory and their introduction of the so-called 3c-4e bond (of which only two of the four electrons are actually bonding and correspond to two collinear 2c-1e bonds in Sugden’s sense, whereas the remaining two electrons correspond to nonbonding or weakly antibonding electrons concentrated on the outer periphery of the molecule).



Figure 1. Robert Eugene Rundle (1915-1963).

In the 1960s and 1970s an extensive literature developed, based on empirical bond-length and bond-angle correlations, which argued for octet expansion, not only in the case of hypervalent species but also for purposes of invoking multiple bond character, via backbonding, in such apparently normal octet species as  $\text{N}(\text{SiH}_3)_3$ ,  $\text{S}_4\text{N}_4$  and  $\text{ClO}_4^-$  (7). At about the same time, quantitative MO calculations on hypervalent species began to appear which tended to support the opposite conclusion and to largely confirm the Rundle-Pimentel picture of the bonding in these species (8).

This debate continued throughout the 1980s and 1990s, when it was fueled by both the discovery of an increasing number of hypervalent species for the second row elements, for which outer d-orbital participation seemed even less likely (9), and by increasingly sophisticated calculations, the majority of which again seemed to support the dominance of the octet rule and the validity of the Rundle-Pimentel model (10), with

the provision that it was necessary to carefully distinguish between the use of “d-functions” to improve computational basis sets, on the one hand, and the use of “d-orbitals” to increase the electron population in the bonds, on the other (11).

One additional consequence of this latter phase was that the appropriateness of Musher’s term “hypervalent” also came under attack. Indeed, in the article in which Musher originally introduced the term, he essentially rejected octet expansion and opted instead for the Rundle-Pimental model, thus implying either that hypervalent species were not truly hypervalent or that the term simply denoted a species that required a bonding scheme other than the traditional Lewis 2c-2e model. In 1984 Paul von Rague van Schleyer suggested the use of the term *hypercoordinate*, rather than hypervalent, to describe such species, as this provided an empirical characterization of their experimentally observed molecular structures without the necessity of having to endorse a particular view concerning the theoretical description of their electronic bonding (12).

Despite the cogency of this suggestion, there are still dissenters (13), and despite the nearly unanimous conclusions of theoretical studies that the octet rule is a valid first approximation for the entire main-block and that it is the traditional Lewis 2c-2e model of covalent bonding which requires modification, octet expansion and the 2c-2e bond still reign supreme in introductory chemistry textbooks, in large part because of the widespread belief that they are a necessary component of the highly successful VSEPR model for the prediction of molecular geometries (14).

### Literature Cited

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