

The Origin of the Metallic Bond

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Question

What is the Origin of the Metallic Bond?

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Answer

The basis of our modern electronic interpretation of metals was laid by the German physicist, Paul Drude (figure 1), and the Dutch theorist, Hendrik Lorentz, in the first decade of the 20th century (1, 2). Both assumed that the weakly bound conduction electrons could be modeled using the classical kinetic theory of gases. Though this “electron-gas” model gave an adequate qualitative rationale of metallic properties, it incorrectly predicted both the heat capacity of metals and the temperature dependence of their electrical conductivity. In addition, it could not explain their magnetic properties (3). In 1928 the German physicist, Arnold Sommerfeld, partially resolved these problems by imposing quantum restrictions on the electron distributions – a lead followed by the Swiss physicist, Felix Block, whose classic paper, published the same year, laid the foundations for modern band theory (4, 5).

The possible relevance of Drude’s original model to the theory of the chemical bond was first pointed out by G. N. Lewis in a paper published in 1913 (6). Though the main thrust of this paper was to argue for the separate existence of a nonpolar (covalent) bond, as distinct from the then generally accepted polar or ionic bond, in its final section, entitled “A Third Type of Chemical Bond,” Lewis further argued that (6):

To the polar and nonpolar types of chemical compound we may add a third, the metallic. In the first type the electrons occupy fixed positions within the atom. In the second type the electrons move freely from atom to atom within the molecule. In the third or metallic type the electron is free to move even outside the molecule ... All known chemical compounds may be grouped in



Figure 1. Paul Karl Ludwig Drude (1863-1906).

the three classes: nonpolar, polar and metallic; except in so far as the same compound may in part or at times fall under two of these groups.

Two years later, the German physicist, Johannes Stark, independently expressed the same idea and also made the first attempt to visualize all three bonding situations (figure 2), though he pictured metals as a rigid lattice of positive ions and electrons rather than as a free-electron gas (7) – a metallic model also advocated by the British physicist, F. A. Lindemann (8). In 1928 the German chemist, Hans Georg Grimm, published his “Dreieckschema” in which he plotted the elements of one row of the periodic table versus another and listed their binary compounds in the resulting

triangular matrix, indicating that the three corners corresponded to salt-like compounds, covalent compounds, and metallic compounds respectively (9). Though usually attributed to the Dutch chemist, Anton van Arkel, the first generalized equilateral bond-type triangle in which the corners corresponded to the ionic, covalent, and metallic bonding extremes, and intermediate bond types were explicitly indicated along the edges, was actually published in the *Journal of Chemical Education* by the American chemists, Conard Fernelius and Richard Robey, in 1935 (10, 11).

The metallic bond has had a very spotty history in the chemical literature. Whereas the thrust of band theory has been the prediction and rationalization of the thermal, electrical, and magnetic properties of metals, chemists are far more interested in bonding models which offer simple correlations between valence-electron counts and both the compositions and structures of possible compounds. Though they have been very successful in developing such correlations in the cases of both the covalent and ionic bonding extremes, similar success in the case of intermetallic compounds and alloys has been almost totally lacking. While one can cite the pioneering attempts of such metallurgists as Hume-Rothery, Laves, and Engels, as well as the brilliant work of the German chemist, Eduard Zintl, on the transition between ionic and metallic bonding, the situation today remains much the same as when it was summarized by Fernelius and Robey in 1935 (9):

The classification of intermetallic compounds is very difficult. Not only are the experimental difficulties great, but as yet no single theoretical or empirical method of treatment has been sufficiently powerful to elucidate more than a portion of the entire field.

More recently there has also been a debate on the very question of whether there is such a thing as a distinct metallic bond, though in the present writer's opinion this was predicated on a misunderstanding of both the nature of idealized bonding extremes and the proper interpretation of bond-type triangles (11). Given these problems, it is perhaps not surprising that 85 years after Lewis first proposed the metallic bond, the vast majority of introductory chemistry texts continue to ignore it and to incorrectly inform their readers that all bonding is either ionic or covalent.

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2. H. A. Lorentz, *The Theory of Electrons and Its Ap-*

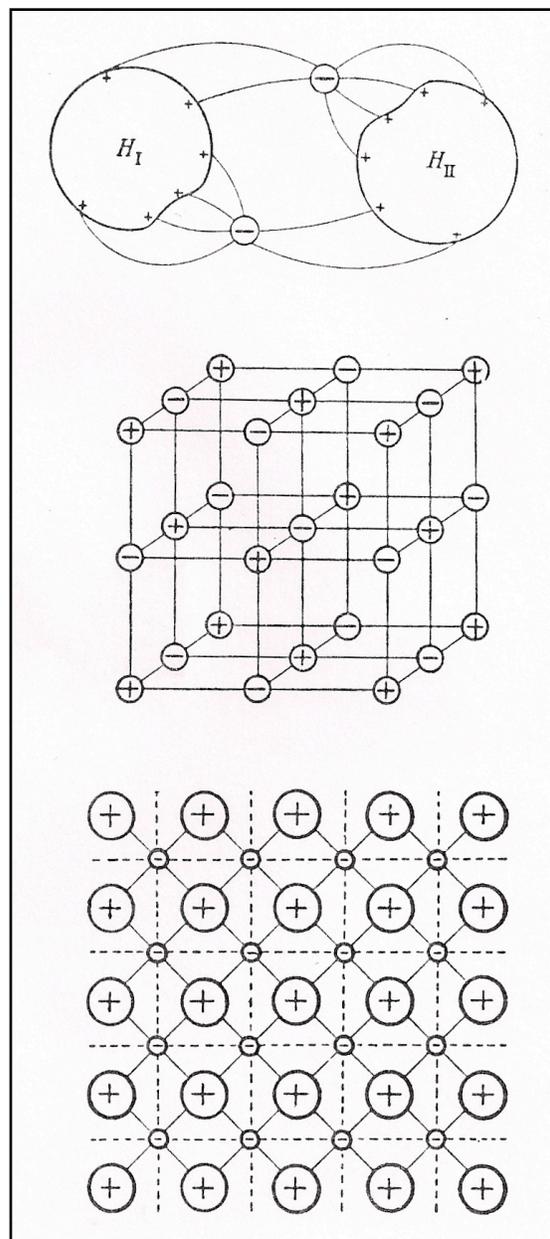


Figure 2. From top to bottom: Stark's 1915 rendition of the shared electron-pair bond in H_2 ; the ionic bond in $NaCl$; and a typical metal viewed as a rigid lattice of positive ions and free electrons (7).

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3. For an historical survey of the contributions of physicist to the theory of metals, see P. B. Allen, W. H. Butler, "Electrical Conduction in Metals," *Physics Today*, **1978**, *31*(12), 44-49.
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THE ORIGIN OF THE METALLIC BOND

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10. W. C. Fernelius, R. F. Robey, "The Nature of the Metallic State," *J. Chem. Educ.*, **1935**, 12, 53-68.
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12. W. P. Anderson, J. K. Burdett, P. T. Czech, "What is the Metallic Bond?," *J. Am. Chem. Soc.*, **1994**, 116, 8808-8809; L. C. Allen, J. F. Capitani, "What is the Metallic Bond?," *Ibid.*, **1994**, 116, 8810; J. C. Schön, "Does the Death Knell Toll for the Metallic Bond?," *Angew. Chem. Int. Ed. Engl.*, **1995**, 34, 1081-1083; L. C. Allen, J. K. Burdett, "The Metallic Bond - Dead or Alive?," *Ibid.*, **1995**, 34, 2003; J. C. Schön, "Reply," *Ibid.*, **1995**, 34, 2004.

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