The Historical Development of the van Arkel Bond-Type Diagram*

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As the biographical sketch by James Bohning in this issue of the *Bulletin* reveals, one of the key events in Ted Benfey's career was his association with Larry Strong at Earlham College and their mutual involvement in the development of the Chemical Bond Approach (CBA) course in the late 1950s and early 1960s (1). CBA was undoubtedly the most innovative of the many attempts at curriculum reform in chemistry which appeared during this period in the United States and elsewhere, and was constructed, as its name implied, around the development of self-consistent models of the chemical bond, starting from a fundamental knowledge of the laws of electrostatics (2).

By the end of Chapter 13, the CBA textbook, *Chemical Systems*, had led students through a presentation of the three basic models used to describe the bonding in covalent, metallic, and ionic materials, and had paused for a reflective overview of what had been accomplished up to that point. The finale of this bonding retrospective was a brief discussion of the possibility of intermediate bond-types using the simple triangular diagram shown in figure 1 (3):

Covalent, metallic, and ionic bonds prove to be a useful way of regarding the structures of many substances. These three types of bonds symbolize three different arrangements of atoms to give structures characteristic of particular substances. The underlying principles for the three types of bonds, however, are based on electrostatics in each type. Each substance represents a system of low energy consistent with the limitations imposed by the Pauli exclusion principle and geometrical relations of the electrons and nuclei which are more fundamental units of structure than are atoms. With the same underlying principles common to all structures, it is not surprising that not all substances can be neatly classified into one of three possible types. The situation can be symbolized by a trigonal diagram [see figure]. The vertices of the triangle represent bond types characteristic of the three extreme bond types. Along each edge of the triangle are represented bond types characteristic of the many substances which do not have extreme bond types.
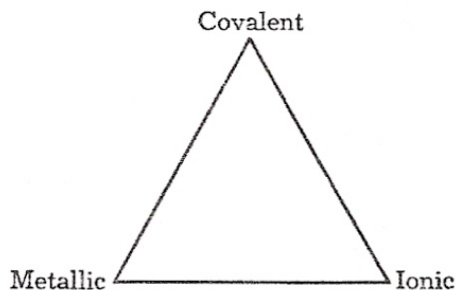

Figure 1. The CBA bond-type triangle.

The use of simple, inclusive diagrams like figure 1 lies at the core of effective teaching. Yet, with the exception of the periodic table, most diagrams of this sort appear without acknowledgment in the average chemistry textbook. Their effectiveness rapidly converts them into community property and, like the inventors of controlled fire, the wheel and metallurgy, their originators appear to be condemned to perpetual anonymity. Given Ted's interests in both chemical education and the history of chemistry, I thought it might not be improper to honor him by rescuing figure 1 from its "ahistorical" fate, both by tracing its early history and reviewing some recent extensions of the diagram which have been made since its appearance in the pages of the CBA textbook nearly three decades ago.

The Three-Fold Way

A necessary prerequisite to the development of any diagram purporting to represent the gradual transition between the three idealized limiting-cases of ionic, covalent, and metallic bonding is, of course, an explicit recognition of the existence of the three limiting-case bond types themselves. The first to receive this recognition was the ionic bond, whose essentials were imperfectly anticipated by the German physicist, Hermann von Helmholtz, in his famous Faraday Lecture of 1881. Arguing that Faraday's laws of electrolysis implied that electricity itself was particulate in nature. Helmholtz opted for a two-fluid theory of electricity in

which particles of matter could combine with mobile particles of both positive and negative electricity. Neutral atoms contained equal numbers of negative and positive electrical particles, whereas positive and negative ions contained an excess of the corresponding electrical particle. Helmholtz further identified the number of excess electrical particles with the valence of the resulting ion, thus, in effect, postulating that all chemical combination was the result of the electrostatic attraction of charged ions, and showed that this model was capable of accounting for the magnitude of the energy release observed in typical chemical reactions.

With the exception of the British physicist, Sir Oliver Lodge, few physicists. and even fewer chemists paid attention to Helmholtz's suggestions until they were revived by J. J. Thomson in conjunction with his ill-fated plum-pudding model of the atom in the period between 1904 and 1907 and reinterpreted in terms of a one-fluid model of electricity in which ionic charge was due to an excess or deficiency of a single mobile negative electrical particle or electron embedded in a nonmobile sphere of positive electrification. Whereas Helmholtz had grafted his electrical particles onto an underlying substratum of classical Newtonian matter, Thomson had reduced matter itself to electricity.

In sharp contrast to the low-key reception accorded Helmholtz, Thomson's version of the polar or "electron transfer" model of bonding excited widespread enthusiasm and predictions of an impending chemical revolution (5). In the United States it led to the development of a polar theory of organic reactivity in the hands of such chemists as Harry Shipley Fry (1908), K. George Falk and John M. Nelson (1909), William A. Noyes (1909), and Julius Stieglitz. In Germany Richard Abegg (1904) successfully connected it with the periodic table, and in 1916 both the American chemist, Gilbert Newton Lewis, and the German physicist, Walther Kossel, reinterpreted it in terms of Rutherford's 1911 nuclear atom model (6).

Quantitative calculations of heats of reaction using the model were made as early 1894 by Richarz and again in 1895 by Hermann Ebert (7). It was successfully applied to the calculation of crystal lattice energies by Max Born and Alfred Lande in the years 1918-1919 (8) and to the calculation of the energies of coordination complexes by Kossel, A. Magnus, Gustav F. Huttig, F. J. Garrick and others in the late teens and 1920s (9). Further refinements and applications were made by Kasimir Fajans, Hans Georg Grimm, and Victor Moritz Goldschmidt in the 1920s, culminating in the publication in 1929 of the monograph *Chemische Binding als Electrostatisch Verschijnsel* (Chemical Bonding as an Electrostatic Phenomenon) by the Dutch

chemists, Anton Eduard van Arkel and Jan Hendrick de Boer (10).

Nonpolar or electron-sharing models of the chemical bond date back to the first decade of the 20th century and the proposals of the German physicist, Johannes Stark (1908), and the German chemist, Hugo Kauffmann (1908). Related models were also suggested by J. J. Thomson (1907), William Ramsay (1908), Niels Bohr (1913), Alfred Parsons (1915) and others (6). However, the overwhelming success of the ionic model and its rapid quantification tended to eclipse these electron-sharing models to such an extent that in 1913 G. N. Lewis felt compelled to write a paper arguing that not only were the physical properties of typical organic compounds incompatible with the ionic model, they also strongly suggested the necessity of a second "nonpolar" bonding mechanism (11). A successful candidate for this nonpolar mechanism was finally provided by Lewis himself in his famous 1916 paper on the electron-pair bond (12). This received widespread attention as a result of its extension and popularization by Irving Langmuir in the period 1919-1921 (Langmuir also introduced the term "covalent bond" in place of Lewis' more cumbersome "electron-pair bond") and with the publication in 1923 of Lewis' classic monograph, *Valence and the Structure of Atoms and Molecules* (13).

Beginning in the mid-1920s, qualitative extensions and applications of the covalent bond were made in the field of organic chemistry by the British chemists, Arthur Lapworth, Robert Robinson, Thomas Lowry, and Christopher K. Ingold, and in the field of coordination chemistry by the American chemist, Maurice Huggins, and the British chemist, Nevil Sidgwick (14). Quantification of the model began two years before the publication of the van Arkel - de Boer book on the ionic model with the advent of wave mechanics and the classic 1927 paper on the H_2 molecule by the German physicists, Walther Heitler and Fritz London (15). However, despite this early start, intensive efforts at quantification of the covalent model really did not get underway until the 1930s and 1940s, via the work of, among others, Linus Pauling, John Slater, Robert Mulliken, Friedrich Hund, and Erich Hückel – or fully a decade after the process was completed for the ionic model. Indeed, these efforts are still a part of the ongoing program in theoretical chemistry.

The initial attraction of both the ionic and covalent models lay in their ability to qualitatively correlate the known compositions and structures of compounds with the number of valence electrons present in the component atoms. These "electron-count correlations" appealed strongly to chemists and are still the basis of much current chemical thought, as witnessed by the
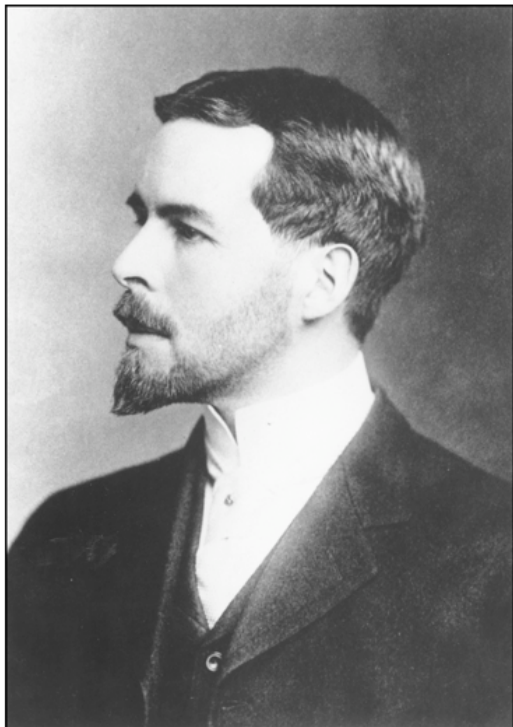
Figure 2. Gilbert Newton Lewis (1875-1946).

more recent development of valence-shell electron-pair repulsion theory (VSEPR) and the current rash of electron counting rules for cluster species (16). Only after these bonding models had proved capable of qualitatively correlating electron counts with composition and structure for significant classes of compounds did chemists exhibit a further interest in their quantification and in their ability to predict cohesive energies and other properties.

The importance of this observation for our survey lies in its implications for the history of the last of our three limiting-case bond types – the metallic bond – since, to this day, chemists have been unable to uncover a significant pattern governing the composition and structure of intermetallic compounds and alloys (many of which are inherently nonstoichiometric), let alone establish simple electron-count correlations for them (17). The resulting failure to attract the attention of chemists has meant that the development of the metallic bonding model has been left largely to solid-state physicists, who, in turn, have tended to stress the explication of thermal, electrical and optical properties, rather than cohesive energies or patterns of composition and structure. In addition, the models which they have developed for this purpose have tended to have a very different conceptual basis than those employed in the chemical literature and it is fair to say that, even today, such concepts as Brillouin zones and pseudopo-

tentials are not part of the everyday working vocabulary of the average chemist. Given this scenario, it also goes without saying that most historical accounts of the development of the chemical bond have little or nothing to say about the evolution of the metallic bond.

Luckily, however, the question of identifying when chemists first recognized the necessity of a separate metallic bonding model is largely independent of the question of whether they did or did not play a significant role in its historical development. Here, as with so much in the history of the chemical bond, we again encounter G. N. Lewis (figure 2), as the earliest explicit recognition in the chemical literature of the necessity of a separate metallic bonding model that I have been able to locate occurs in the same 1913 paper in which Lewis so forcibly argued for the separate existence of the nonpolar or covalent bond. In the final section of this paper, entitled "A Third Type of Chemical Bond," Lewis noted that (11):

To the polar and non-polar 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 the three classes: non-polar, polar and metallic; except
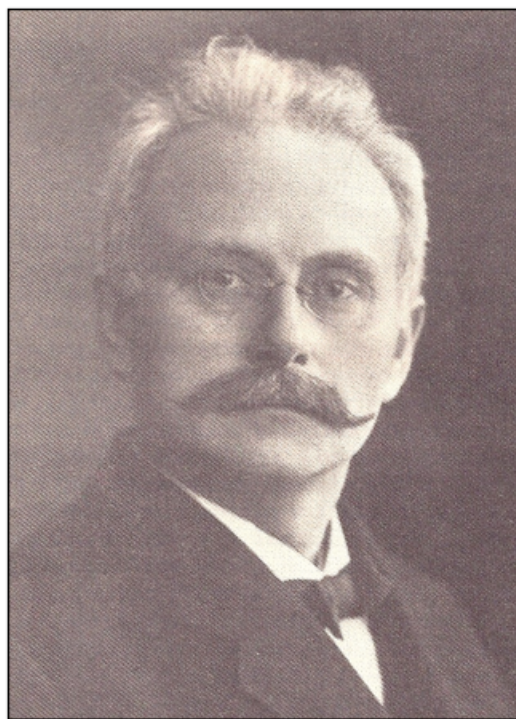

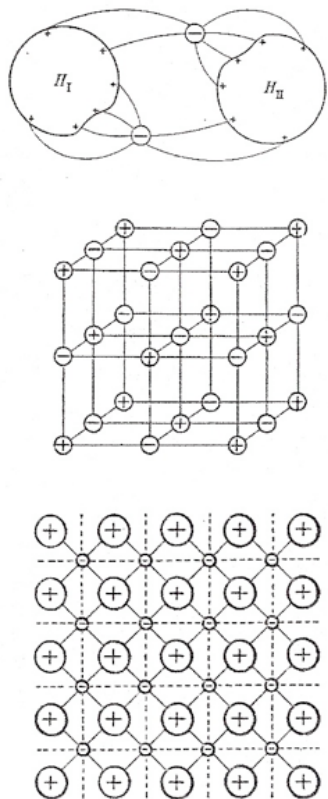Figure 4. Johannes Stark (1874-1957).

Figure 4. Stark's 1915 representation (from top to bottom) of the shared-electron bond in dihydrogen, the structure of NaCl as a lattice of positive and negative ions, and the structure of a metal as a lattice of positive ions and free electrons.

in so far as the same compound may in part or at times fall under two of these groups.

The first attempt to visualize all three bond types (figure 4) appeared two years after Lewis' paper in part three of Johannes Stark's monograph *Prinzipien der Atomdynamik: Die Elektrizitat im chemischen Atom* (18). This appears to have been an independent development, since Stark (figure 3) does not cite Lewis. Also recall that, though Lewis argued for the necessity of a nonpolar bond in his 1913 paper, he did not propose a specific model for that bond until 1916, a year after the appearance of Stark's monograph. As already noted, Stark and the German organic chemist, Hugo Kauffmann, had both argued for an electron-sharing model of the nonpolar chemical bond as early as 1908 and, in the case of simple. single-bonded diatomics, had correctly inferred that this bond must correspond to a pair of shared electrons. However, both Kauffmann – who was seduced by the special problems surrounding the bonding in benzene and the theories of partial valence proposed by the German chemist, F. K.

Johannes Thiele – and Stark – who elected to follow only the qualitative dictates of classical electrostatics – failed to extend this conclusion in a useful way to more complicated molecules. and opted instead for a wide range of multicentered one-, two- and three-electron bonds. The final result was far too flexible to allow for meaningful electron-count correlations and it remained for Lewis to take the results of classical valence theory seriously and to successfully develop the consequences of the conclusion that the chemical bond of the 19th-century chemist was "at all times and in all molecules merely a pair of electrons held jointly by two atoms" (13).

A second attempt to visualize Lewis' three bond types, as well as weaker intermolecular attractions, using Bohr's dynamic atom model, was made eight years later by Carl Angelo Knorr in one of the first German papers to describe Lewis' electron-pair bond (figure 5). Like Lewis, Knorr recognized the possibility of transitional bond types and was able to further correlate the various limiting-case models with the growing body of solid-state structural data that had been obtained from X-ray crystallography since the publication of Lewis' original paper (19):

These four extremely different bond types, between which there exist countless transitions and which can be schematically illustrated in the following manner [see figure] also correspond to four different kinds of crystal lattice, namely the ionic lattice (cesium fluoride), the atom lattice (diamond), the molecular lattice (ice), and the metallic lattice (sodium).

The free-electron model for the metallic bond suggested by Lewis, Stark, and Knorr had, in fact, been around for more than a decade by the time Lewis wrote his paper, having been introduced by the physicists, Paul Drude (1900) and Hendrick Antoon Lorentz (1909), in order to account for the electrical and optical properties of metals (20). Such a model is immediately suggested by the high electrical conductivity of metals
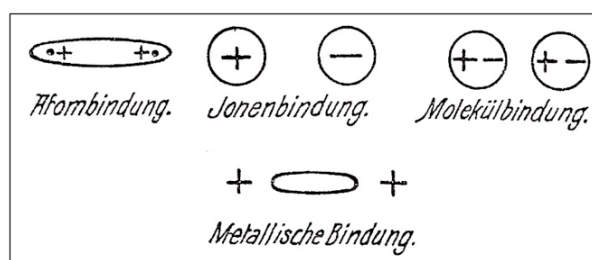

Figure 5. Carl Angelo Knorr's 1923 representation of the three limiting bond types and weak intermolecular attractions (Molekülbindung) in terms of localized Bohr orbits.

and is still invoked in the crude form used by Lewis, Stark, and Knorr in the modern freshman chemistry text where it is usually coupled with a description of the crystal structures of typical metals. However, the examples used are always simple substances and all mention of the eccentricities of intermetallic compounds and alloys is carefully avoided. Indeed, it is fair to say that in English-speaking countries this topic has never formed a major part of the mainstream chemical literature, having instead been largely consigned to the metallurgical literature. The same, however, does not appear to be true of the German chemical literature, where a concerted effort to establish electron-counting correlations for intermetallic species has remained a part of the province of the inorganic chemist, as exem-

Figure 7. Examples of Grimm's triangular binary combination matrices.

that of the German chemist, Hans August Georg Grimm (figure 6), who has already been mentioned in connection with his work on the development of the ionic model (22). Beginning in 1928, Grimm published a series of six articles dealing with the systematization and classification of binary compounds (23-28). In order to trace out the pattern of ionic, covalent, and metallic bonding throughout the periodic table, Grimm constructed both intra- and inter-row binary combination matrices for the elements, with the elements placed in order of increasing group number on the *x*-axis and decreasing group number on the *y*-axis (figure

Figure 6. Hans Georg Grimm (1887-1958).

plified by the significant contributions made by such chemists as Eduard Zintl and Ulrich Dehlinger throughout the 1930s (21). In keeping with this assertion, it is also of interest to note that, despite Lewis' prescience in his 1913 paper, no mention of the metallic bond can be found in either his 1916 paper or in his famous monograph of 1923.

The Grimm-Stillwell Bond-Type Diagram

The first attempt to construct a triangular diagram linking the three limiting-case bond types appears to be

Figure 8. Grimm's generalized triangular binary combination matrix or "Dreieckschema."

7). Each square of the resulting triangular matrix represented a real or potential binary compound, whose predominant bonding character was indicated by means of a characteristic cross-hatch pattern. Complete coverage of the entire periodi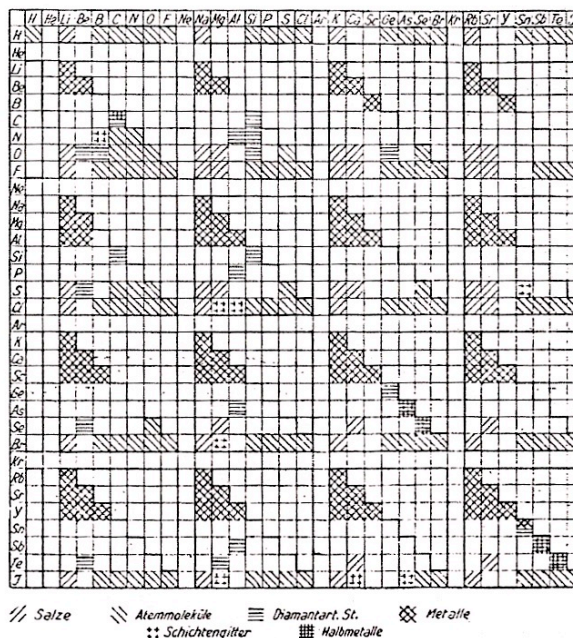c table required the construction of a separate matrix for each possible intra- and inter-row combination, and Grimm attempted to assemble these diagrams into a master diagram or so-called periodic table of binary compounds (26). Moreover, since all of the matrices gave similar results, he also summarized

this pattern in the form of a generalized "Dreieck-schema" which linked the three limiting-case bond types to one another via a characteristic pattern of intermediate bond types (figure 8).

Of particular interest is Grimm's use of plus and minus signs along the diagonal of his "Dreieckschema" in order to indicate the predominant electrochemical character of the component elements in the resulting binary compounds. Thus metal-metal or electropositive-electropositive combinations leading to metallic
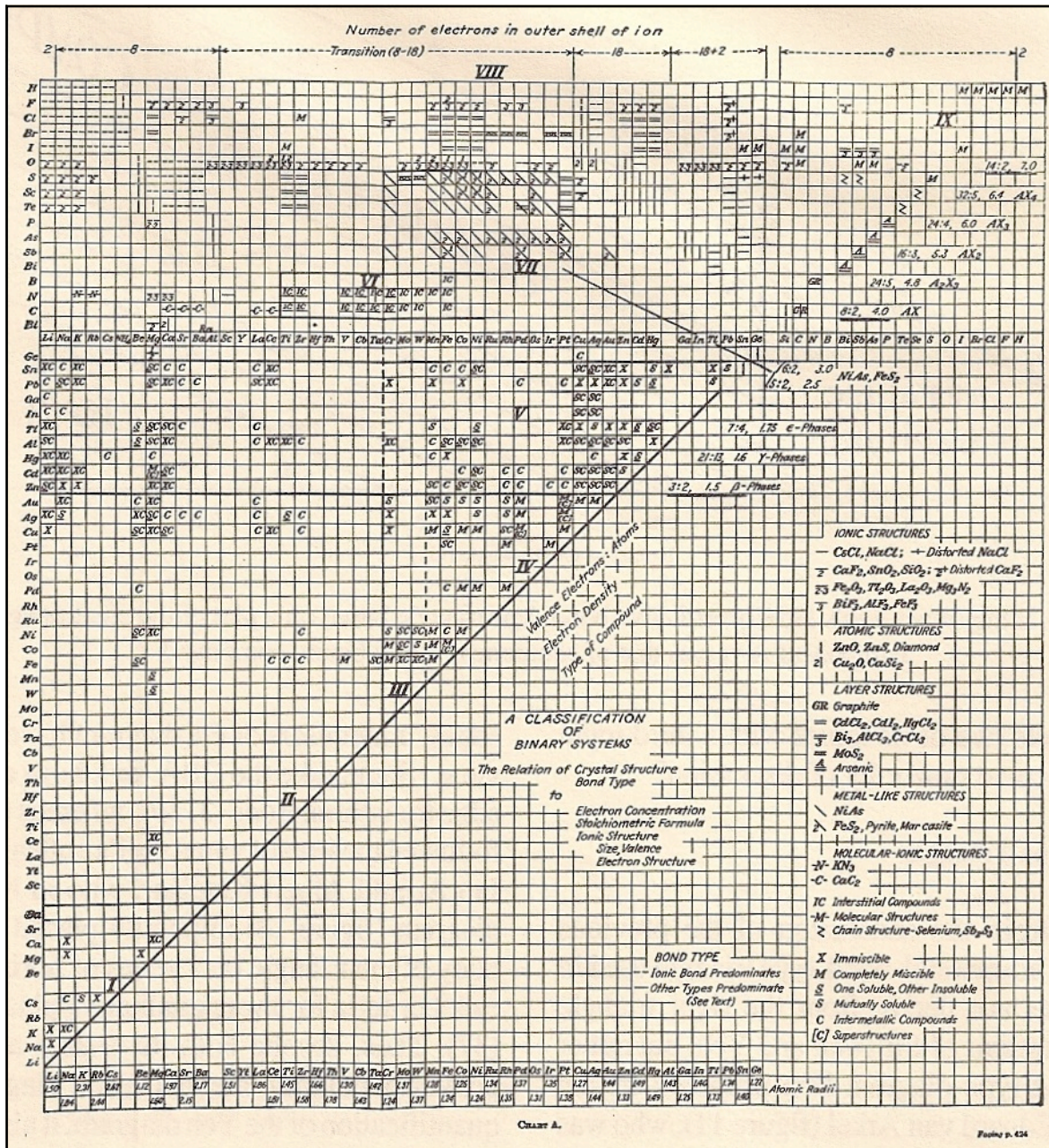
Figure 9. Charles Stillwell's 1936 bond-type matrix for binary compounds.

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bonding were indicated by the symbol +/+, metal-nonmetal or electropositive-electronegative combinations leading to ionic bonding were indicated by the symbol +/-, and nonmetal-nonmetal or electronegative-electronegative combinations leading to covalent bonding were indicated by the symbol -/-.

Like all chemists since Berzelius, Grimm was aware that the electronegativity of the elements increased as they became increasingly nonmetallic. He was further aware that electronegativity always increased on moving across a period of the periodic table (Indeed, in recognition of this fact, the German chemist, Lothar Meyer (29), had suggested the term "electrochemical period" in 1888 as a way of characterizing the conventional choice of periods in the periodic table) so, in effect, each of Grimm's diagrams represented a qualitative plot of the electronegativity of element A versus the electronegativity of element B in the resulting binary compounds A_aB_b. As long as he restricted each axis to a single period of the periodic table, Grimm could be confident that the elements were placed in order of either increasing (*x*-axis) or decreasing electronegativity (*y*-axis). However, in the absence of a quantitative electronegativity scale, he was unable to intermix elements from different periods of the periodic table on the same axis, and thus collapse all of his diagrams into a single quantitative master diagram,

An attempt at the latter step was taken by the American chemist, Charles Stillwell, in 1936 (30), He constructed a gigantic triangular master matrix by placing all of the elements along both the *x*- and *y*-axes in the order of their decreasing "metallicity" (figure 9). Though Stillwell did not explicitly spell out how he determined his metallicity order, we can infer his reasoning from an examination of his axes. These listed the elements by group from left to right across the periodic table, beginning with all of the alkali metals and ending with all of the halogens. Within each group, the nonmetals were generally listed from the bottom to the top of the group (save for N, B and Al, which were interdispersed), whereas the metals were listed from the top to the bottom of each group. With the exception of the ordering of the metals within each group and the listing of hydrogen as the least metallic element, this order roughly corresponds to the qualitative order given by Lothar Meyer a half-century earlier for the variation of electronegativity across the periodic table (29).

Like Grimm, Stillwell also attempted to characterize the binary combinations corresponding to each square of his matrix as metallic, ionic, or covalent, though his notation was much more complicated and intermixed both structural and bond-type criteria. However, despite the imperfections of his metallicity

order, he was able to sort the binary compounds in his matrix into regions characteristic of each bond and/or structural type.

The Yeh Bond-Type Triangle

The first quantitative electronegativity scale – Pauling's thermochemical scale – did not appear until 1932 (31). Though this preceded the publication of Stillwell's diagram and most of Grimm's publications, the scale would have been of little use to them in constructing their bond-type diagrams as the original paper reported electronegativity values for only ten elements. Despite the fact that this number had climbed to 33 by the time the first edition of *The Nature of the Chemical Bond* appeared in 1939, it was still far too small to quantify the kind of massive overview envisioned by these authors (32).

The first attempt to construct a bond-type diagram based on a quantified electronegativity scale was made by the Chinese chemist, Ping-Yuan Yeh, in a short note published in *The Journal of Chemical Education* in 1956 (33). Using the electronegativity values reported in Pauling's introductory text, *General Chemistry*, which Yeh was using in his freshman course, Yeh produced his bond-type diagram by plotting the electronegativity of element A versus that of element B for both binary compounds, A_aB_b, and for simple substances (figure 10). Though Yeh was apparently unaware of the earlier work of Grimm and Stillwell, his bond-type diagram was in fact a partial quantification of Stillwell's triangle – partial because Pauling's text was still reporting electronegativity values for only 33 of the elements – indeed, the same values as had appeared 17 years earlier in the first edition of *The Nature of the Chemical Bond*. The apparent difference in the orientation of Stillwell's diagram was, of course, due to the fact that his binary combination matrix was redundant, with each binary compound appearing twice, once above and once below the 45° diagonal, and Stillwell had arbitrarily chosen to eliminate the bottom rather than the top half.

Yeh's presentation of his diagram also reflected some of the biases of American chemical education mentioned earlier. Thus he divided his diagram into three sharp regions – in response to the ever-present demands of students that, in the interests of exams-manship, they be given a black and white answer to the question of when a material is or is not ionic, covalent, or metallic – even though he was fully aware that in reality there were "no sharp transitions from one type to another." Even more revealing was the fact that the region of the diagram labeled "metallic compounds" contained no specific examples other than simple sub-

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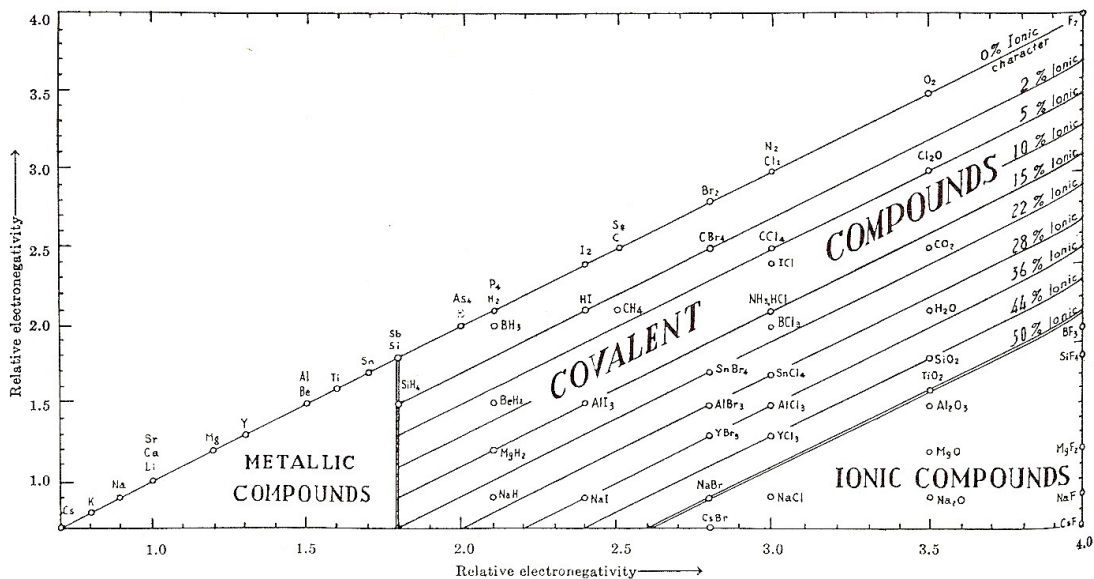
Figure 10. Ping-Yuan Yeh's 1956 quantitative bond-type triangle based on a plot of the EN of component A versus that of component B in a binary compound.

stances, again reflecting the absence of any substantive discussion of these compounds in most introductory textbooks (34).

Despite its simplicity and attractiveness, the Yeh diagram appears to have been an educational dead end, as I have never encountered an example of its use in a textbook. This oversight is almost certainly traceable to the cause just mentioned – after all, why would a textbook be interested in using a diagram which explicitly connects two of its topics with a third topic which it has already deemed unworthy of discussion?

The van Arkel Bond-Type Triangle

As may he surmised from the conclusion of the previous section, the qualitative, equilateral bond-type triangle used in the CBA textbook does not derive from the right triangle characteristic of the diagrams of Stillwell and Yeh, but rather from a qualitative bond-type diagram first proposed by the Dutch chemist, Anton Eduard van Arkel (figure 11), who was mentioned earlier in connection with the publication of his landmark book on the ionic bonding model (35). The diagram in question, which is shown in figure 12, first appeared in van Arkel's 1941 textbook, *Moleculen en Kristallen* (Molecules and Crystals) (36), and unlike the Stillwell-Yeh diagram, it has been successful in attracting the attention of at least a few textbook authors (3, 37-43).

As can be seen from the figure, van Arkel's original diagram had no quantitative coordinates. He merely guessed the location of each compound based on an

intuitive estimate of its relative ionic and metallic character. In addition, he showed examples of progressive changes only on the outer edges of the diagram, thus leaving open the question of whether he viewed the diagram merely as three line segments with their ends joined or as a true solid triangle with compounds

Figure 11. Anton Edward van Arkel (1893-1976).

Figure 12. Van Arkel's 1941 bond-type triangle.

of intermediate character located within the triangle as well as along its edges. Later users of the diagram have adopted both points of view. Some, like the CBA text, have continued to show only edge transformations (3, 39), whereas others (38, 40-43) have followed the lead of van Arkel's colleague, the Dutch chemist Jan Arnold Albert Ketelaar, who, in his 1947 version of the diagram (figure 13) implicitly placed compou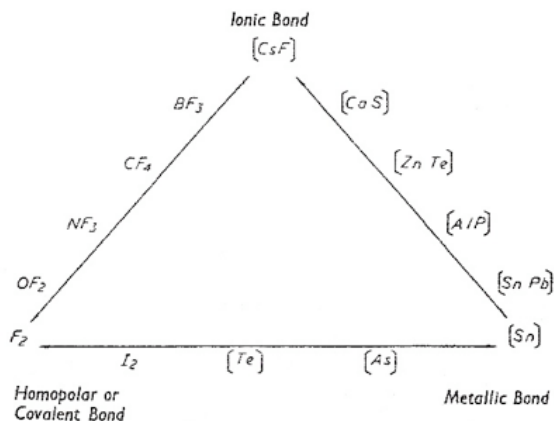nds within the body of the triangle on a series of horizontal lines, though the exact criteria for these qualitative placements were not given (37). Thus, despite both its greater aesthetic appeal and its greater popularity, the van Arkel diagram not only lacks the quantification of the Yeh diagram. it also suffers from a certain ambiguity of interpretation.

Quantifying the van Arkel Diagram

Both of these defects can be overcome by means of a quantitative form of the van Arkel diagram which I first developed in 1980, and which I have been using
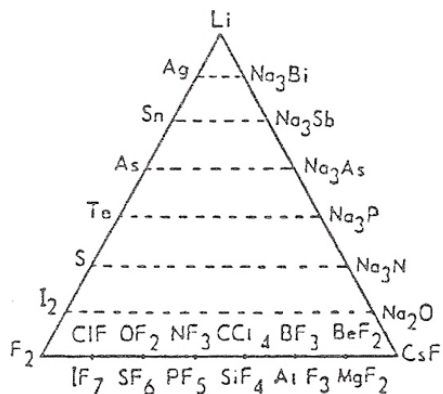
Figure 13. Ketelaar's 1947 version of the van Arkel bond-type triangle.

for over a decade in both my inorganic and freshman chemistry courses (44). The diagram in question is obtained by plotting a parameter for each binary compound which characterizes the polarity or ionicity of its bonds versus a parameter which characterizes the co-valency (or, conversely. the metallicity) of its bonds. The ionicity parameter (I) is simply defined as the difference in the electronegativities (ΔEN) of the two elements, A and B, in a binary compound, A_aB_b, irrespective of stoichiometry:

$$I \; = \; \Delta EN \; = \; (EN_B - EN_A) \qquad [1]$$

This parameter will have a large value in the case of the low EN_A - high EN_B combinations characteristic of ionic compounds and a small value for the high EN_A - high EN_B and low EN_A - low EN_B combinations characteristic of covalent and metallic compounds respectively.

Likewise, the covalency parameter (C) is defined as the average of the electronegativities (EN_{av}) of the two elements, A and B, in a binary compound, A_aB_b, irrespective of stoichiometry:

$$C \; = \; EN_{av} \; = \; (EN_A + EN_B)/2 \qquad [2]$$

This parameter will have a large value in the case of the high EN_A - high EN_B combinations characteristic of covalent compounds and a small value in the case of the low EN_A - low EN_B combinations characteristic of metallic compounds. It will have an intermediate value for the low EN_A - high EN_B combinations characteristic of ionic compounds. Just as I can be associated with the asymmetry of the bond, so C can be associated with its localization. As C decreases, the bonding will become less directional and more diffuse – in short, more metallic.

A plot of these two parameters for a variety of binary compounds and alloys is shown in figure 14. As can be seen, the compounds all lie within an equilateral triangle, with the ionic, covalent, and metallic extremes at each vertex. Just as in the case of the Yeh diagram, compounds of intermediate character, representing the transition between one extreme and another, lie along the edges and within the body of the triangle. For completeness, I have also included simple substances in the plot in order to have a transition along the edge joining the covalent and metallic extremes. These can be artificially viewed as a special type of compound in which both of the elements have the same EN. Equation 1 automatically assigns them an ionicity of zero and their covalency, as defined by equation 2, is identical to their electronegativity. Since the noble gases do not undergo self-linkage, they cannot be thought of as being com-

Figure 14. A quantified van Arkel diagram based on a plot of ionicity versus covalency for a variety of binary compounds, alloys, and simple substances.

pounds even in this artificial sense and hence are excluded from the diagram. However, their binary compounds with other elements (e.g., XeO_4, KrF_2, etc) are included. Because of the intense radioactivity of the element francium and the resulting nonavailability of its compounds for display and demonstration purposes, I have taken cesium as the archetypical metallic species and cesium fluoride as the archetypical ionic species. Since, as already mentioned, neon does not undergo homocatenation, difluorine (F_2) serves as the archetypical covalent species.

Closer examination of the figure shows that, in sharp contrast to the horizontal lines of Ketelaar's diagram, the compounds of each element lie on two diagonal lines which meet at the location of the corresponding simple substance on the *x*-axis, the left branch of which contains those compounds in which the element in question is the more electronegative component and the right branch those compounds in which it is the more electropositive component. The only exceptions are the compounds of fluorine, for which the electropositive branch is missing, and the compounds of cesium, for which the electronegative branch is missing, their remaining branches forming the two ascending sides of the triangle.

In making the plot in figure 14 and those which follow in figures 15-17, I have used the absolute values of a slightly modified version of the electronegativity scale introduced by the Russian chemists, Martynov and Batsanov, in 1980, based on an averaging of the successive ionization energies for an element's valence electrons (45). The more familiar Allred-Rochow scale works just as well at the level of correlation used in freshman chemistry, provided that it is supplemented by published estimates for the electronegativities of the

noble gases (46).

The definitions of the *I* and *C* parameters given in equations 1 and 2 also reveal that the van Arkel and Yeh diagrams are related via a simple series of coordinate transformations. Aside from the greater aesthetic appeal of the resulting equilateral triangle, the major advantage of using the more complex *I/C* coordinates versus the simpler EN_A/EN_B coordinates of the Yeh diagram, lies in the fact that the corresponding *ΔEN* and EN_{av} combinations can be loosely correlated with energy terms used in approximate quantum mechanical treatments of the bonding in binary solids, such as the well-known charge-transfer (*C*) and homopolar (E_h) parameters of Phillips (47).

Figures 15-17 illustrate some additional uses of the diagram obtained by plotting limited groups of compounds subject to additional external constraints. Thus figure 15 shows a plot of a series of compounds that are both isostoichiometric (l:1 or AB) and isoelectronic (total of eight valence electrons). As can be seen, the compounds are nicely sorted into regions corresponding to their crystal structures. Because structure depends on stoichiometry and valence-electron counts, as well as bond character, it is necessary to fix two of these parameters before varying the third. This is an important limitation on the use of the van Arkel triangle and one which most introductory treatments of chemical bonding unhappily ignore. Thus it is not uncommon to find freshman textbooks implying that a one to one correlation exists between bond type and the physical properties of binary solids, such as melting point and conductivity, irrespective of their stoichiometry and valence-electron counts, though in actual fact, the first of these properties depends much more strongly on structure type than bond type (48).

Figure 15. A structure-sorting map for 1:1 AB compounds composed of main-block elements having eight valence electrons.
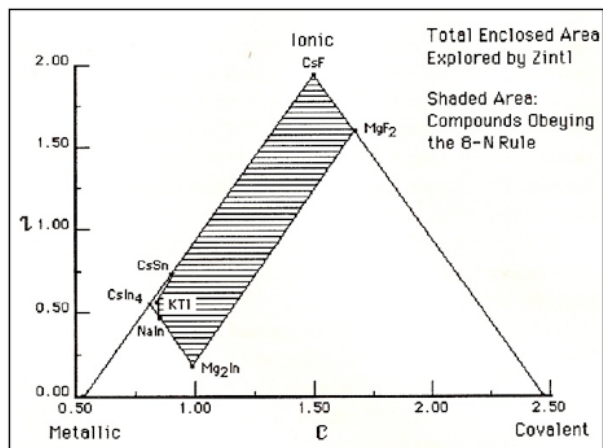
Figure 16. The van Arkel characterization of over 516 Zintl phases representing the transition between ionic and metallic bonding.

Similar structure-sorting maps can he obtained for other isostoichiometric classes of compounds (AB_2, AB_3, etc.). Again, the ΔEN and EN_{av} combinations can be loosely, correlated with the various combinations or pseudopotential radii that have been widely used as structure-sorting parameters by solid-state physicists (49).

Figure 16 gives an example of how I use the diagram in my inorganic course to locate characteristic groups of compounds before discussing the details of their descriptive chemistry. The shaded area on the triangle represents the location of over 516 "Zintl phases," first investigated by the German chemist. Eduard Zintl, in the 1930s and, more recently, by the late Herbert Schafer of the Technische Hochschule in Darmstadt as part of a systematic study of the transition between ionic and metallic bonding in binary compounds. All of the compounds within this region have structures which can he rationalized via an electron-count correlation known as the generalized 8-N rule, which is based, in turn, on our traditional ionic and covalent bonding models (50). Attempts to move further down the diagram toward the metallic vertex result in the formation of typical alloy phases whose structures no longer obey the 8- N rule.

Finally. figure 17 gives an example of how I use the diagram in my freshman chemistry course. In this case samples of the materials in question are shown to the students and a quick and dirty test of their conductivity is made (or simply provided, in the case of gases) with a probe-buzzer-battery tester. A plot of the compounds and simple substances on the triangle shows that those with detectable conductivities are located near the metallic vertex, that metallic appearance does not necessarily correlate with conductivity (i.e., solid I_2), and that both the **I** and **C** parameters are needed in

order to accurately sort the compounds and simple substances into conductors and nonconductors (i.e., solid NaCl doesn't conduct despite having a lower EN_{av} than solid SiC).

Conclusion

It was Henry Bent, I think, who sagely observed that all chemical demonstrations automatically illustrate all of the principles of chemistry, since every principle is involved, to a greater or lesser degree, in our understanding of the phenomenon in question. Our use of a demonstration to illustrate a single principle is an artifice produced by intentionally focusing the students' attention on only one aspect of the phenomenon. The same is true to a lesser degree of the diagrams and illustrations that we use in our textbooks and in our classrooms. As we have seen in the case of the CBA bond-type triangle, when restored to their historical context, such diagrams can serve as microexamples of the evolution of chemistry itself. In our particular case this history also serves as elegant testimony to the creativity and originality of Larry Strong, Ted Benfey and the many other teachers who played a role in the development of the CBA program and its accompanying text.

References and Notes

* A paper published in a special issue of *The Bulletin for the History of Chemistry* honoring the life and career of the American chemist and historian, Otto Theodor Benfey.
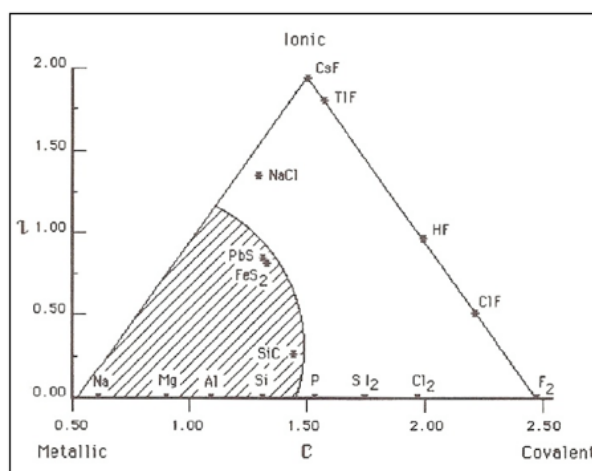

Figure 17. A plot of a selection of compounds and simple substances used as part of a demonstration in freshman chemistry to illustrate the development of incipient metallic character in binary compounds. Only substances within the shaded area show a detectable conductivity using a crude probe-buzzer-battery conductivity detector.

1.   J. J. Bohning, "From Stereochemistry to Social Responsibility: The Eclectic Life of Otto Theodor Benfey," *Bull. Hist.. Chem.*, **1992-93**, *13/14*, 4-16.

2.   P. D. Hurd, *New Directions in Teaching Secondary School Science*, Rand McNally: Chicago, IL. 1969; and W. H. Brock, *The Norton History of Chemistry*, Norton: New York. NY. 1993. Chapter II.

3.   CBA, *Chemical Systems*, McGraw-Hill: New York. NY, 1964. pp. 593-594.

4.   H. von Helmholtz, "The Modern Development of Faraday's Conception of Electricity," *J. Chem. Soc., * **1881**, *38*, 277-304. In actual fact, Helmholtz's suggestions merely replaced one puzzle with another. In the course of providing an electrostatic explanation of why atoms attracted one another to form molecules, he implicitly introduced the necessity of having to postulate a new force in order to explain the attraction between the underlying particles of matter and the particles of both positive and negative electricity.

5.   For a typical example of this somewhat premature enthusiasm, see R. K. Duncan, *The New Knowledge: A Simple Exposition of the New Physics and the New Chemistry in their Relation to the New Theory of Matter*, Barnes: New York, NY, 1908.

6.   These proposals and extensions are discussed in great detail in A. N. Stranges, *Electrons and Valence: Development of the Theory, 1900-1925*, Texas A&M Press: College Station, TX, 1982. This is a well-documented history of the electronic theory of bonding up to 1925 with an excellent bibliography. The only point on which it is weak is in its coverage of the ionic model during the period 1916-1923, largely because of its overemphasis on the emergence of Lewis' electron-pair bond.

7.   These early calculations are summarized in S. Arrhenius, *Theories of Chemistry,* Longmans: London, 1907, pp. 61-64.

8.   Summaries of the work of Born and Lande can be found in reference 10, chapter 3, and in M. Born, *Atomtheorie des festen Zustandes*, Teubner: Leipzig, 1923. A more personal account is given in M. Born, *My Life: Recollections of a Nobel Laureate*, Scribner: New York, NY, 1975, pp. 181-183 and 188-190.

9.   Summaries of the development of the electrostatic theory of coordination compounds can be found in reference 10, Chapter 8, and in R. W. Parry, R. N. Keller, "Modern Developments: The Electrostatic Theory of Coordination Compounds," in J. C. Bailar, Ed., *The Chemistry of Coordination Compounds*, Reinhold: New York, NY, 1956, Chapter 3.

10. A. E. van Arkel, J. H. de Boer, *Chemische Bindung als Electrostatisch Verschijnsel*, Centen: Amsterdam, 1929. This was translated into German as *Chemische Bindung als electrostatische Erscheinung*, Hirzel: Leipzig, 1931, and into French as *La valence et l'electrostatique*, Alcan: Paris, 1936. No English translation was ever made and all references are to the 1931 German edition. The first extensive English account of the literature dealing with the quantitative ionic model did not appear until 1931 and dealt only with the Born-Lande theory of ionic lattice energies – a small fraction of the material covered by the van Arkel - de Boer book. See J. Sherman, "Crystal Energies of Ionic Compounds and Thermochemical Applications," *Chem. Rev.*, **1931**, *11*, 93-170.

11.   G. N. Lewis, "Valence and Tautomerism," *J. Amer. Chem. Soc.*, **1913**, *35*, 1148-1455.

12.   G. N. Lewis, "The Atom and the Molecule." *Ibid.*, **1916**, *38*, 762-785.

13.   G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, Chemical Catalog Co: New York, NY, 1923. This was translated into German as *Die Valenz und der Bau der Atome und Molekule*, Vieweg: Braunschweig, 1927. For the role of Langmuir, see reference 6 and W. B. Jensen, "Abegg, Lewis, Langmuir and the Development of the Octet Rule," *Chem. Educ.*, **1984**, *61*, 191-200.

14.   For a good account of the British School of organic reactivity, see W. H. Brock, reference 2, Chapter 15. For applications to coordination chemistry, see R. W. Parry and R. N. Keller, "Modern Developments: The Electron Pair Bond and the Structure of Coordination Compounds,"reference 9, Chapter 4.

15.   W. Heitler, F. London, "Wechselwirkung neutraler Atome und homoopolare Bindung nach der Quanteumechanik," *Zeit. Physik.*, **1927**, *44*, 455-472.

16.   For VSEPR, see R. J. Gillespie, I. Hargitai, *The VSEPR Model of Molecular Geometry*, Allyn and Bacon: Boston, 1991; for cluster electron-counting rules, see S. M. Owen, "Electron Counting in Clusters: A View of the Concepts," *Polyhedron*, **1988**, *7*, 253-283.

17.   Electron-count correlations have been established for certain groups of intermetallic compounds and alloys, such as the well-known Hume-Rothery rules, but their range of application is quite limited.

18.   J. Stark, *Prinzipien der Atomdynamik: Die Electrizität im chemischen Atom*, Teil 3, Hirzel: Leipzig, 1915, pp. 120, 180, 193-195.

19.   C. A. Knorr, "Eigenschaften chcmischer Verbindungen und die Anordung der Elektronenbahnen in ihren Molekülen," *Z. anorg. Chem.*, **1923**, *129*, 109-140.

20.   H. A. Lorentz, *The Theory of Electrons and Its Application to the Phenomena of Light and Radiant Heat*, Teubner: Leipzig, 1909; and P. Drude, "Zur Elektronentheorie der Metalle," *Ann. Phys.*, **1900**, *1*, 566-613; *Ibid.*, **1900**, *3*, 369-402; *Ibid.*, **1902**, *7*, 687-692. Drude also references an even earlier free-electron model proposed by E. Reiche. An overview of this early work can also be found in K. Baedeker, *Die elektrischen Erscheinungen in metallischen Leitern*, Vieweg: Braunschweig, 1911.

21. For lead-in references see E. Zintl, "Intermetallische Verbindungen," *Angew. Chem.*, **1939**, *52*, 1-6; U. Dehlinger,

"Die Chemie der metallischen Stoffe in Verhaltnis zür klassischen Chemie," *Ibid.*, **1934**, *47*, 621-624; W. Klemm, "Intermetallische Verbindungen," *Ibid.*, **1935**, *48*, 713-723; and F. Weibke, "Intermetallische Verbindungen," *Z. Elektrochem.*, **1938,** *44*, 209-221 and 263-282.

22. U. Hofmann, "Hans Georg Grimm zum 70. Geburtstag," *Z. Elektrochem.*, **1958**, *62*, 109-110.

23. H. G. Grimm. "Allgemeines tiber die verschiedenen Bindungsarten," *Ibid.*, **1928**, *34*, 430-437.

24. H. G. Grimm and H. Wolff, "Uber die sprungweisc Änderung der Eigenschaften in Reihen chemischer Verbindungen," in P. Debye, Ed., *Probleme der Modernen Physik*, Hirzel: Leipzig, 1929, pp. 173-182.

25. H. G. Grimm, "Zur Systematik der chemischen Verbindungen vom Standpunkt der Atomforschung, zugleich über einige Aufgaben der Experimentalchemie," *Naturwiss.*, **1929**, *17*, 535-540 and 557-564.

26. H. G. Grimm, "Das Periodische System der chemischen Verbindungen vom Typ A_mB_n," *Angew. Chem.*, **1934**, *47*, 53-58.

27. H. G. Grimm, "Die energetischen Verhaltnisse im Periodischen System der chemischen Verbindungen vom Typ A_mB_n," *Ibid.*, **1934,** *47*, 593-561.

28. H. G. Grimm, "Wesen und Bedeutung der chemischen Bindung," *Ibid.*, **1940**, *53*, 288-292.

29. L. Meyer, *Modern Theories of Chemistry*, Longmans: London, 1888, pp. 154, 516.

30. C. W. Stillwell, "Crystal Chemistry: 1. A Graphic Classification of Binary Systems," J. *Chem. Educ.*, **1936**, *13*, 415-419; also C. W. Stillwell, *Crystal Chemistry*, McGraw-Hill: New York, NY, 1938, Chapter 5 and foldout chart in appendix.

31. L. Pauling, "The Nature of the Chemical Bond. IV. The Energy of Single Bonds and the Relative Electronegativity of Atoms," *J. Am. Chem. Soc.*, **1932,** *54*, 3570-3582.

32. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1939, pp. 58-75.

33. P-Y Yeh, "A Chart of Chemical Compounds Based on Electronegativities," *J. Chem. Educ.*, **1956**, *33*, 134.

34. The fist edition of Pauling's *General Chemistry* (1947) contained no reference to intermetallic compounds and the nature of metallic bonding. Though the chapter on metallic bonding and structure added to the second edition (1954) did contain a passing reference to several binary compounds of silver and strontium, Yeh was unable to plot these compounds because Pauling did not provide an *EN* value for silver.

35. E. W. Gorter, R. C. Romeyn, "A. E. van Arkel: On the Occasion of his Retirement from the Chair of Inorganic Chemistry at Leyden University," *Chem. Weekblad*, **1965**, *60*, 298-308.

36. A. E. van Arkel, *Moleculen en Kristallen*, van Stockum: s'Gravenhage, 1941. An English translation of the second Dutch edition appeared as *Molecules and Crystals*, Butterworths: London, 1949. A second English edition of the enlarged fourth Dutch edition appeared in 1957. All references are to the first English edition in which the diagram appeared on page 205.

37. J. A. A. Ketelaar, *Chemical Constitution*, 2nd ed., Elsevier, Amsterdam, 1958, p. 21. The first Dutch edition was published in 1947. Ketelaar overlapped with van Arkel at Leyden in the period 1934-1941 during which he collaborated with van Arkel's group on X-ray crystallography. Recently Allen has tried to quantify the horizontal cuts in Ketelaar's diagram by placing compounds of similar average *ΔEN* on each horizontal, with the average increasing from the bottom to the top of the triangle. This limits the triangle to compounds formed among the elements of a single row of the periodic table and does not fill the entire area of the triangle. See L. C. Allen, "Extension and Completion of the Periodic Table," *J. Am. Chem. Soc.*, **1992**, *114*, 1510-1511.

38. K. B. Harvey, G. B. Porter, *Introduction to Physical Inorganic Chemistry*, Addison-Wesley: Reading, MA, 1963, pp. 1 and 4.

39. M. B. Ormerod, *The Architecture and Properties of Matter: An Approach Through Models*, Arnold: London, 1970, p. 103.

40. D. M. Adams, *Inorganic Solids*, Wiley: New York, NY, 1974, p. 106.

41. W. L. Jolly, *Modern Inorganic Chemistry*, McGraw Hill; New York, 1984, p. 265.

42. K. M. Mackay, R. A. Mackay, *Introduction to Inorganic Chemistry*, 4th ed., Blackie: Glasgow, 1989, p. 80.

43. J. D. Lee, *Concise Inorganic Chemistry*, 4th ed., Chapman and Hall: London, 1991, p. 31.

44. First presented at an all-departmental "Symposium on Chemical Bonding" held at the University of Wisconsin, Madison, WI, in July of 1980. Originally I used metallicity, *M*, defined as $EN_{av}(F)$ - *C* for my *x*-axis, but have use *C* alone since 1990 as I find that students are better able to understand it. A more complete presentation is given in W. B. Jensen, *Electronic Equivalency and the Periodic Table: Lectures on the Structural Similitude of Atoms, Simple Substances, and Binary Compound*s, University of Cincinnati: Cincinnati, OH, 1991, Lectures 12-14.

45. A. I. Martynov, S. S. Batsanov, "A New Approach to the Determination of the Electronegativity of Atoms," *Russ. J. Inorg. Chem.*, **1980**, *25*, 1737-1739.

46. M. C. Ball, A. H. Norbury, *Physical Data for Inorganic Chemists*, Longman: London, 1974, pp. 14-18 and references cited therein for estimates of the electronegativities of the noble gases. These are quite simple to calculate using the Martynov-Batsanov definition.

47. J. C. Phillips, *Bonds and Bands in Semiconductors*, Academic Press: New York, 1973. A correlation between *ΔEN* and *C* is given on page 39. A plot (available on request) of EN_{av} versus E_h gives a similar degree of correlation.

48. For a summary of the early literature dealing with

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the relationship between bond type, structure type, and physical properties, see Stillwell (1938), reference 30, pp. 165-177. A more recent example is given in E. C. Lingafelter, "Why Low Melting Does Not Indicate Covalency in MX_4 Compounds," *J. Chem. Educ.*, **1993**, *70*, 98-99.

49. J. K. Burdett, G. D. Price, S. L. Price, "Factors Influencing Solid-State Structure – An Analysis Using Pseudo-potential Radii Structural Maps," *Phy. Rev. B*, **1981**, *24*, 2903-2912.

50. H. Schafer, B. Eisenmann, W. Miller, "Zintl Phases: Transitions Between Metallic and Ionic Bonding," *Angew. Chem. Internat. Edit.*, **1973**, *12*, 9-18.

Note Added in Proof

I have recently discovered that an equilateral bond-type triangle similar to that of van Arkel was given as early as 1935 in W. C. Fernelius and R. F. Robey, "The Nature of the Metallic State," *J. Chem. Educ.*, **1935**, *12*, 53-68. Since this article was reprinted in R. K. Fitzgerel, W. F. Kieffer, Eds., *Supplementary Readings for the Chemical Bond Approach*, Journal of Chemical Education: Easton, PA, 1960, it, rather than van Arkel's book, is the most likely origin of the diagram which appeared in the CBA text, though the van Arkel book is better known.

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