A Quantitative van Arkel Diagram

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In 1941 the Dutch chemist, Anton Eduard van Arkel, proposed an attractive triangular diagram (Fig. 1) to represent the progressive transition between the three limiting-cases of ionic, covalent, and metallic bonding (1). Given its pedagogical appeal, it is rather surprising that so few textbook authors have made use of this representation (2–7), perhaps because chemistry texts seldom provide a substantive discussion of intermetallic compounds and alloys.

As can be seen from an examination of Figure 1, 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 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 have continued to show only edge transformations (4, 5); whereas, others (3, 6–7) have followed the lead of van Arkel's colleague, the Dutch chemist, Jan Arnold Albert Ketelaar, who in his 1947 version of the diagram (Fig. 2) implicitly placed compounds within the body of the triangle on a series of horizontal lines, though again the exact criteria for these qualitative placements were not given (2).

More recently, Allen (Fig. 3) has attempted to rationalize explicitly the horizontal lines in Ketelaar's version of the original diagram (8).[1] Though Allen's description of his placement procedure is confined to a short and largely un-

Figure 1. The original 1941 version of van Arkel's bond-type triangle (1).

informative figure caption, he appears to have constructed his triangle, using only the elements in row three of the periodic table, by placing the elements in question at equal intervals along the base of the triangle in order of increasing configuration energy (which is Allen's euphemism for electronegativity). He then divides the triangle into equally spaced horizontals. On the first horizontal he places at equal intervals the binary compounds corresponding to each pair of elements on the base–centering it between the symbols for these elements. Thus, MgAl appears on the first horizontal half way between Mg and Al on the base; AlSi half way between Al and Si, etc. On the remaining horizontals he places at equal intervals the binary compounds formed by combining the metal from the left binary on the horizontal below it with the nonmetal

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[1]Allen has been aware of my approach to the quantification of the van Arkel diagram since 1990 through both private correspondence and conversation.
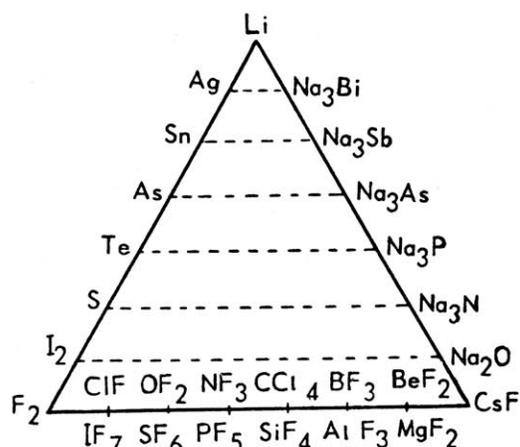
Figure 2. Ketelaar's 1947 version of the bond-type triangle showing his horizontal cuts through the body of the triangle (2).
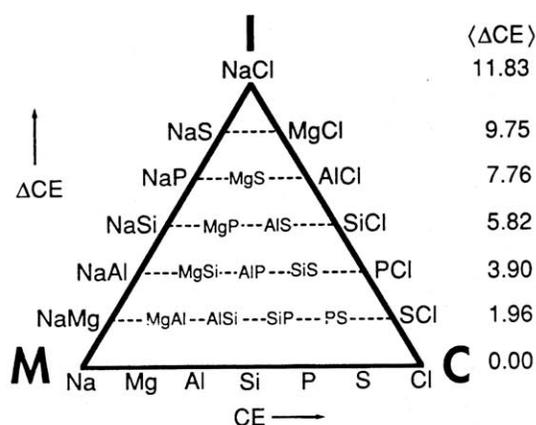
Figure 3. Allen's 1992 version of a semi-quantitative van Arkel triangle (8). The symbols I, M, and C stand for the ionic, covalent, and metallic bonding extremes and should not be confused with the *I* and *C* symbols used in Figures 4–7. Allen does not give the specific formulas of actual compounds and his composite symbols are intended to represent all possible compositions for the binary combinations in question. Explanations of the other labels in the diagram are given in the text.

from the right binary on the horizontal below it. Thus, MgP appears half way between MgSi and AlP, etc. This placement procedure is repeated until one reaches the top of the triangle. Though Allen characterizes this procedure as a "quantification of the van Arkel–Ketelaar triangle", it is really only semi-quantitative. No coordinate system appears on the diagram because all of the points in the triangle have been qualitatively placed at equal distances in both the vertical and horizontal directions using the binary combination recipe just outlined. The label "CE →" along the bottom of the triangle applies only to the elements along the base and is intended to indicate the direction of qualitative increase. Likewise, the label "<ΔCE>", to the right of the triangle, is not a coordinate system, but rather a label indicating the average value of ΔCE for the binary compounds on each horizontal. The label "ΔCE ↑" to the left of the triangle is apparently an error for "<ΔCE>↑", since the compounds on each horizontal have variable individual ΔCE values, as can be seen in the case of those located on the first horizontal:

NaMg MgAl AlSi SiP PS SCl

ΔCE: 2.51 1.89 2.29 2.00 2.10 1.66   <ΔCE> = 1.96 (1)

and it is only the average <ΔCE> values of the horizontals that increase monotonically on moving up the triangle.

The purpose of this note is to share with the readers of *the Journal* a quantitative form of the van Arkel diagram which I first proposed in 1980 and which I have been using for over a decade in both my inorganic and Freshman courses.[2] This diagram not only removes the ambiguities present in the earlier qualitative forms of the triangle, it also subsumes Allen's semi-quantitative version as a special case. 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 covalency (or, conversely, the metallicity) of its bonds. The ionicity parameter, I, is simply defined as the difference in the electronegativities of the two elements, A and B, in a binary compound, A_aB_b, regardless of stoichiometry:

$$I = \Delta EN = (EN_B - EN_A) \qquad (2)$$

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 of the two elements, A and B, in a binary compound, A_aB_b, regardless of stoichiometry:

$$C = EN_{av} = \frac{(EN_A + EN_B)}{2} \qquad (3)$$

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.[3]

A plot of these two parameters for a variety of binary compounds and alloys is shown in Figure 4. As can be seen, the compounds all lie within an isosceles triangle, with the ionic, covalent, and metallic extremes at each vertex. Intermediate cases, 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 2 automatically assigns them an ionicity of zero and their covalency, as defined by eq 3, is identical to their electronegativity. Because the noble gases do not undergo self-linkage, they cannot be thought of as being compounds even in this artificial sense and, hence, are excluded from

[2]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 $EN_{av}(F_2) - C$ for my x-axis, but I have used C alone since 1990 because I find that students are better able to understand it.

[3]Some proponents of band theory object to the use of the term "metallic bond", preferring instead to talk about the metallization of the covalent bond. However, most Freshman texts still use a distinct and separate limiting-case model for metallic bonding (i.e., the "electron gas" model). Consultation of 25 recent Freshman texts showed that all of them used the term "metallic bond" as an index entry, as do about half of the recent inorganic texts. For this reason, as well as the fact that the term has meaning for other models of the metallic state, such as Pauling's metallic bond and Oliver Johnson's interstitial metallic model, I have continued to use the term in describing the van Arkel triangle.

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 Fr and the resulting nonavailablity of its compounds for display and demonstration purposes, I have taken Cs as the archetypical metallic species and CsF as the archetypical ionic species. Because, as already mentioned, Ne does not undergo homocatention, F_2 serves as the archetypical covalent species. Closer examination of the figure shows that, in sharp contrast to the misplaced emphasis on horizontal lines in the versions of the diagram given by both Ketelaar and Allen, 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 F, for which the electropositive branch is missing, and the compounds of Cs, for which the electronegative branch is missing, their remaining branches forming the two ascending sides of the triangle. Allen's special triangle for the compounds and simple substances of row three now appears as a smaller triangle within this larger, more general, bond-type triangle, and his horizontal lines now spread into horizontal bands due to the quantitative placement of the compounds along the *y*-axis in the actual order of their increasing individual ΔEN values.

In making the plots in Figures 4–7 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 (*9*). 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[4]. Other combinations of electronegativity will produce similar diagrams, the most simple being a straightforward plot of EN_A versus EN_B first given by Yeh in 1956 (*11*), which is actually a generalization and quantification of an even earlier bonding diagram or "Dreieckschema" given by the German chemist, Hans Georg Grimm, in the late 1920's.[5] However, such plots lack the aesthetic appeal of the isosceles van Arkel triangle. In addition, the ΔEN and EN_{av} combinations can be correlated loosely with energy terms used in approximate quantum mechanical treatments of the bonding in
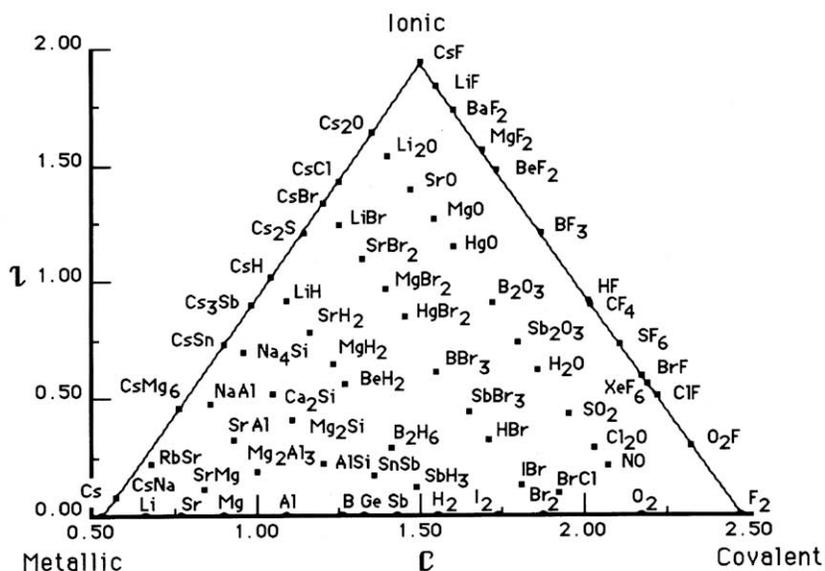
Figure 4. A quantified van Arkel diagram based on a plot of the ionicity parameter ($I = \Delta EN$) versus the covalency parameter ($C = EN_{av}$) for a variety of binary compounds, alloys, and simple substances.
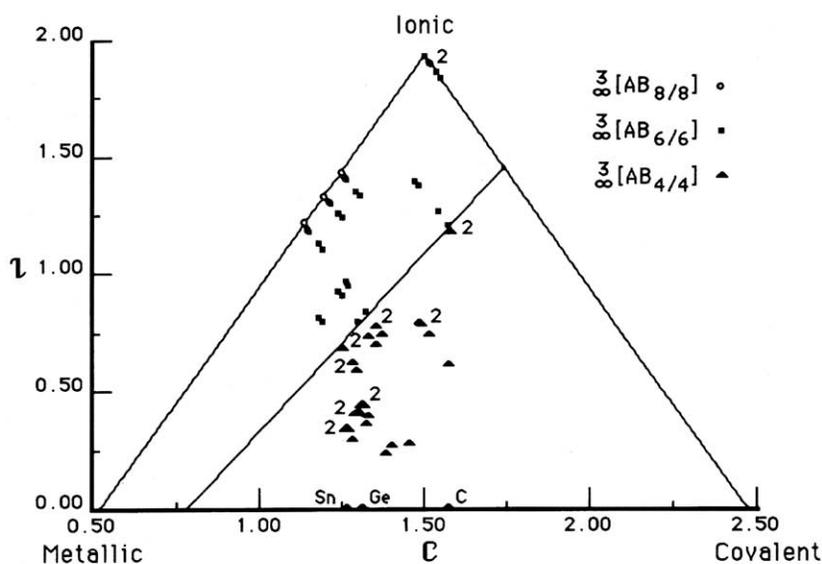
Figure 5. A structure-sorting map for 1:1 AB binary compounds having eight valence electrons.

binary solids, such as the well-known charge-transfer (*C*) and homopolar (E_h) parameters of Phillips (*14*).[6]

Figures 5–7 illustrate some additional uses of the diagram obtained by plotting limited groups of compounds subject to additional external constraints. Thus, Figure 5 shows a plot of a series of compounds that are both isostoichiometric (1:1 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. Similar structure-sorting maps can be 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 of pseudopotential radii that have been widely used as structure-sorting parameters by solid-state physicists (*15*).

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[4]See reference *10* and references cited therein for estimates of the electronegativities of the noble gases. These are quite simple to calculate using the Martynov–Batsanov definition.

[5]Grimm obtained his diagrams by constructing 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. A separate diagram was required for each intra- and inter-row combination. See reference *12*.

[6]For a more detailed history of these diagrams, see reference *13*.

Figure 6 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 1930's and, more recently, by the late Herbert Schäfer of the Technische Höchschule in Darmstadt, as part of a systematic study of the transition between ionic and metallic bonding in binary compounds.

Finally, Figure 7 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 combination. A plot of the compounds and simple substances on the triangle shows that those with detectable conductivities are located near the metallic vertex (shaded area), that metallic appearance does not necessarily correlate with conductivity (i.e., solid I_2), and that both parameters are needed to sort accurately 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).

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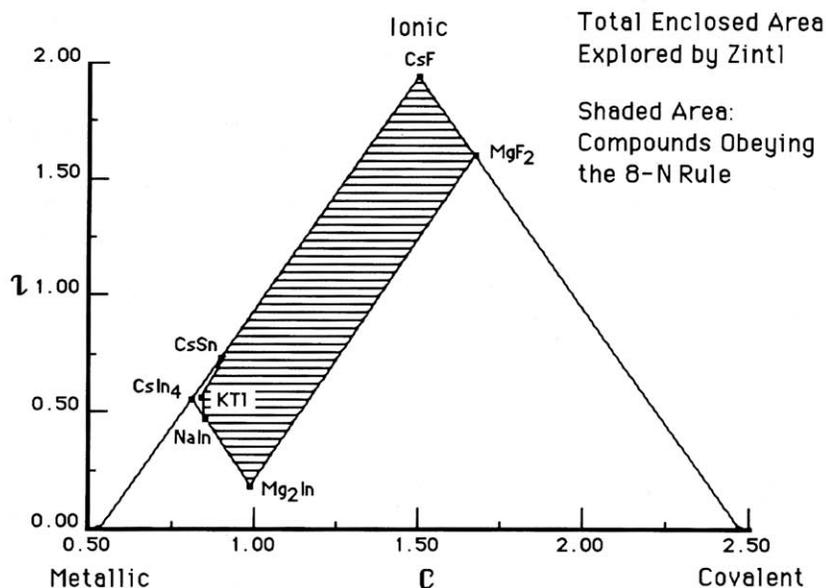
Figure 6. The van Arkel characterization of over 516 "Zintl phases" first investigated by the German chemist, Eduard Zintl, in the 1930's and, more recently, by the late Herbert Schäfer of the Technische Höchschule in Darmstadt, as part of a systematic study of the transition between ionic and metallic bonding in binary compounds.
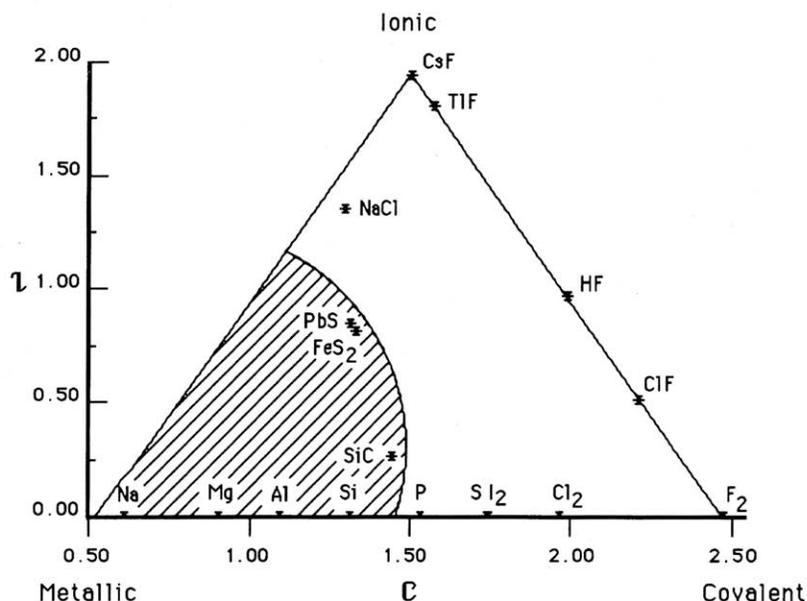
Figure 7. A plot of a selection of compounds and simple substances used as part of a demonstration in Freshman chemistry to illustrate the development of incipient metallic properties in binary compounds. Compounds and simple substances in the shaded region show detectable conductivity with a crude probe-buzzer-battery conductivity detector, whereas those outside the shaded region do not.