

# Logic, History, and the Chemistry Textbook

## II. Can We Unmuddle the Chemistry Textbook?

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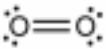
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*The following is the second of three invited keynote lectures given at the 57th annual summer conference of the New England Association of Chemistry Teachers held in August of 1995 at Sacred Heart University in Fairfield, Connecticut. Lecture I has appeared in an earlier issue of the Journal (1).*

Our interest in the classification of the various theoretical concepts and models of modern chemistry, presented in Lecture I, lies not only in our desire to better understand their interrelationships and underlying assumptions, but also in the use of this classification to aid us in detecting and clarifying errors and ambiguities in our presentation of these concepts and models and in the consequences which this classification has for how we teach these concepts and models to our students.

Relative to both of these functions, the most important pedagogical lesson to be extracted from Lecture I is the logical necessity of carefully distinguishing between the molar, molecular, and electrical levels of discourse in chemistry. Unhappily, this is also the point on which most modern textbooks falter, as not only do they generally fail to explicitly point out the existence of these three levels, they normally proceed to randomly mix them together throughout the book. Take, for example, the three textbook descriptions of dioxygen gas given in Table 1, each of which corresponds to one of our three levels of discourse. Not only is the sequence listed in the table the most logical order for developing a progressively more abstract description of dioxygen gas, it also happens to correspond, as we will see in Lecture III, to the actual historical evolution of our views concerning this most important of chemical substances. Yet how frequently is this order scrambled in the average textbook and the students shown a Lewis diagram or a molecular orbital configuration for dioxygen gas before they are told anything about its appearance, molar properties, natural occurrence, preparation, or chemical reactivity?

**Table 1. Dioxygen Gas as Viewed at the Molar, Molecular and Electrical Levels of Discourse**

| Level      | Description  |
|------------|--|
| Molar      | A colorless, odorless, paramagnetic, highly reactive gas, essential for most life, composing 21% of the atmosphere by volume, mp = 54.8 K, bp = 90.2 K, density = 1.43 kg/m <sup>3</sup> at 273 K. |
| Molecular  | A linear, double-banded, diatomic O <sub>2</sub> molecule having a molecular weight of 31.98 amu.  |
| Electrical | <br>or<br>$[2s\sigma]^2[2s\sigma^*]^2[2p\pi_x]^2[2p\pi_y]^2[2p\sigma]^2[2p\pi_x^*]^1[2p\pi_y^*]^1$              |

To further illustrate these problems, we will first look at some examples, taken from both the introductory and the advanced inorganic textbook literature, in which the random mixing of concepts from each of these distinct levels of discourse leads to illogical and, at times, even incorrect results. This will be followed by examples of how a failure to explicitly identify concepts and definitions with their corresponding levels of discourse has resulted in the propagation of historically outdated definitions and vocabulary in the textbook and has led to a proliferation of conflicting claims about the nature and sphere of application of certain models and teaching diagrams in the current chemical and educational literature.

Some of you may be asking yourselves why, given that I am addressing a room full of chemistry teachers, I just don't outline an introductory chemistry course based on the logic table given in Lecture I? Of course, it goes without saying that I have been progressively modifying my own introductory chemistry course along these lines, but this is still very much "a work in progress". In addition, I am loath to tell others how they must teach chemistry. My job, as I indicated in Lecture I, is rather to enhance and stimulate your own understanding of chemistry. How you translate that enrichment into specific classroom activities for your students will naturally vary from teacher to teacher, depending on the level of the course being taught and on the degree of control which you are given over both the content and mode of presentation.

### Detection of Logically Flawed Definitions and Concepts

As our first example, consider the following typical definitions of physical versus chemical change taken from the third edition of a well-known introductory chemistry text for health science majors (2):

In a physical change, the form of the matter is changed, but not its chemical properties. The tearing of paper, melting of ice, or dissolving of salt and sugar in water are all examples of physical changes ... A chemical change involves electron cloud interactions between the atoms of the matter involved.

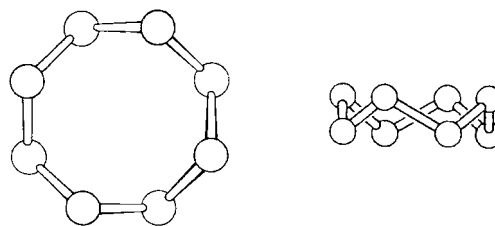
Setting aside some very real doubts about whether the processes cited in this quotation are really chemical or physical, the important point is that these two definitions are incommensurate with one another—or, in common parlance, they amount to an attempt to compare apples with oranges. The processes cited to illustrate physical change are all described at the molar level, whereas the definition given for chemical change is at the electrical level. The problem of how to distinguish a chemical versus a physical change at either the molar or at the electrical level is simply not addressed, making the above definitions operationally useless to a student

who is asked decide whether the rusting of iron (a molar description) or the van der Waals attraction between two xenon atoms (an electron cloud interaction) are chemical or physical in nature.

The supposed distinction between chemical and physical changes has formed a part of the opening chapters of virtually every introductory chemistry text since the late 18th-century and you would think that, after 225 years of practice, we would have finally gotten it right. The complication, of course, is that these 225 years also happen to correspond to the very time period which saw the elaboration of the molar chemistry of the 18th century via the addition of both the molecular and electrical levels of discourse. Though modern chemistry is certainly more complete and more reductionistic than late 18th-century chemistry, it is also more complicated in that it offers many more levels of discourse and hence many more alternative ways of viewing a given phenomena. And with this conceptual diversity also comes an increased opportunity for confusion via an incompatible mixing of these alternatives.

A slightly different twist to this question can be found in a debate which took place in the *Journal of Chemical Education* in 1970. In the February issue of that year, Walter Gensler of Boston University published an article entitled "Physical versus Chemical Change" in which he argued that such a "distinction is not really meaningful [and that] in fact, as now presented, it is frequently indefensible and confusing" (3). Gensler's critique of these concepts was made at the molecular and, to a lesser degree, at the electrical level, and essentially involved an analysis of various supposed examples of chemical versus physical change in terms of the question: "Is a chemical bond made or broken in the process?"

In the October issue, Laurence Strong of Earlham College wrote a rejoinder entitled "Differentiating Physical and Chemical Changes" in which he argued that these were indeed legitimate and useful distinctions which could be specified at the molar level in terms of four operational criteria (Table 2), which he called identity, mixing, discontinuity, and invariance (4). Strong was quite explicit about the fact that he and Gensler were using two distinct levels of discourse (which Strong labeled "theoretical" and "experimental" rather than molecular and molar), so there is no question here of confusing levels as there was in the case of our textbook ex-



Rhombic Sulfur  $\leftrightarrow$  Monoclinic Sulfur  
95.5° C

Figure 1. Top (left) and side (right) views of the structure of the octasulfur rings found in both the rhombic and monoclinic forms of sulfur.

ample. Nor do I think that there is a question of whether one of these authors is right and the other wrong. Both presented cogent and, in many ways, equally convincing arguments.

What is of most importance is that this debate raises the very real question of whether the same distinction can be made with equal force at all three levels of discourse—or, put another way, are there perfectly valid distinctions at one level of discourse (e.g., the molar) which disappear at another level (e.g., the molecular)? I think the answer to this question is a definite yes, and it further underscores the importance of avoiding such potential confusion by carefully characterizing the models and concepts that we use in chemistry in terms of their location in the logic table introduced in Lecture I.

As a second example, this time at the advanced inorganic level, consider the use of the term "polymorphism", briefly mentioned in Lecture I. According to a well-known dictionary of chemistry, this term refers to (5):

A phenomenon in which a substance exhibits two or more different crystal forms ... Polymorphism is restricted to the solid state. Polymorphs yield identical solutions, liquids, and vapors.

At first glance this would appear to be a molar definition, though in fact, like our previous example, it involves an intermixing—albeit a much less obvious one—of both molar and molecular criteria. The key to disentangling this admixture is to note that its use of the term "substance" violates the standard molar definition of a pure substance as a material having a fixed and reproducible set of specific properties at a given temperature and pressure by asserting that in the solid state, at least, the same substance can have two or more different sets of specific molar properties (i.e., not only different crystal forms but also, as a result, different densities and solubilities, and, at times, even different optical, electrical, and magnetic properties). Thus no one would ever define isomers as different forms of the *same substance*. Rather they are defined as different substances which happen to have identical composition, but otherwise totally distinct properties.

This curious use of the word substance in our definition of polymorphism is in fact based on an outdated 19th-century molecular interpretation of the phenomenon—an interpretation which, in turn, assumes that all materials, whether in the solid, liquid, or gaseous state, are composed of discrete molecules (6). Isomers were thought to correspond

Table 2. Strong's Molar Criteria for Differentiating Chemical versus Physical Changes

| Criterion     | Behavior  |
|---------------|---|
| Identity      | In chemical change the identity of the products is determined by the identity of the reactants                  |
| Mixing        | In chemical change mixing of the reactants is essential   |
| Discontinuity | In chemical change there is a discontinuity in the properties of the reactants versus those of the products     |
| Invariance    | In chemical change product properties are invariant to changes in initial temperature, pressure and composition |

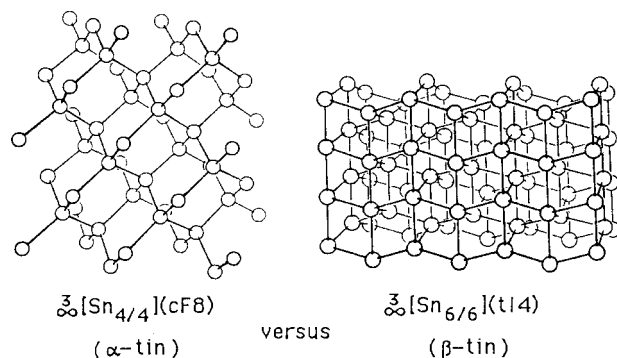


Figure 2. The structures of  $\alpha$ -tin (left) and  $\beta$ -tin (right).

to substances having discrete molecules of identical composition but differing intramolecular structure. Because these differences resided within the molecule itself, each isomer corresponded to a different substance. Furthermore, these differences persisted as long as the molecules remained intact. As a result, the distinctions between one isomer and another frequently survived such processes as melting, vaporization, and dissolution.

Polymorphs, on the other hand, were assumed to contain molecules of identical composition and identical intramolecular structure, their differences being due instead to differences in the intermolecular packing of these molecules in the solid state. Since the identical molecule was present in each polymorph, they were considered to be merely different forms of the same substance. Furthermore, once these differences in intermolecular structure were destroyed via melting, vaporization, or dissolution, all differences between the polymorphs likewise disappeared (Table 3).

The classic example of polymorphism corresponding to these definitions is the case of rhombic versus monoclinic sulfur, both of which contain the identical  $\text{S}_8$  molecule in the form of a puckered eight-member ring (Fig. 1), but differing packing arrangements of these molecules within the crystal lattice (7). Indeed, the distinction which these definitions make between isomers, on the one hand, and polymorphs, on the other, is not unlike the classic distinction between chemical and physical changes discussed earlier. Interconversion of isomers involved a change in intramolecular structure and thus corresponded to a transformation of one substance into another or to a chemical change. Interconversion of polymorphs involved a change in intermolecular structure only and thus corresponded to a change in form rather than substance or to a physical change.

The problem with these interpretations is that their underlying premise—that all materials must contain discrete molecules—has been known to be incorrect for the last 80 years. Indeed, X-ray crystallography has shown that the vast

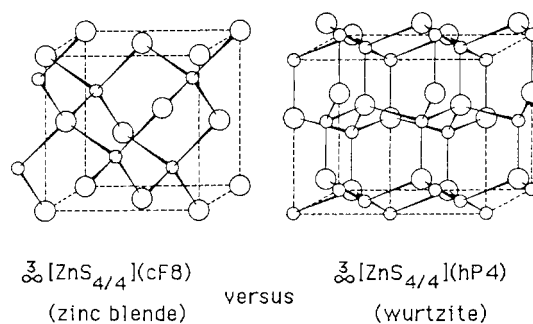


Figure 3. The structures of zinc blende (left) and wurtzite (right).

majority of inorganic solids do not contain discrete molecules at all but rather infinitely extended framework, layer, and chain structures. As a consequence, it is now known that the differences between many classic examples of polymorphism actually reside in a fundamental difference in the structures of these infinitely extended molecules, rather than in a difference in the intermolecular packing of discrete, but otherwise identical, molecular units.

Thus the differences between the  $\alpha$ - and  $\beta$ -polymorphs of tin are ultimately traceable, as we saw in Lecture I, to a difference in their bonding topologies,  $\alpha$ -tin being composed of an infinitely extended framework structure with 4/4 coordination and  $\beta$ -tin being composed of an infinitely extended framework structure with distorted 6/6 coordination (Fig. 2). Hence these two polymorphs are, in effect, topological isomers of one another.

Likewise, the difference between wurtzite and zinc blende, the two most common polymorphs of zinc sulfide, is also ultimately traceable to a difference in molecular structure. Both substances contain infinitely extended framework structures with 4/4 coordination and hence have identical bonding topologies (Fig. 3). However, their structures are neither superimposable nor are they mirror images of one another. Thus, in effect, they correspond to diastereomers or geometric isomers of one another.

Finally, it is of interest to note that quartz crystals can exist in both left- and right-handed forms (Fig. 4). I have never seen these listed as polymorphs, which suggests that the traditional definitions of just what constitutes a difference in crystal structure fail to take chirality into account. Needless to say, the underlying molecular structures of these two forms have identical bonding topologies, corresponding to an infinitely extended framework structure with 4/2 coordination, but are, otherwise, nonsuperimposable mirror images of one another (Fig. 5). Hence they correspond to enantiomers or chiral isomers of one another. *In all three of these examples, the differences observed in the solid state fail to*

Table 3. The 19th-Century Molecular Interpretation of Isomerism versus Polymorphism

| Class      | Same Composition? | Same Intramolecular Structure? | Same Intermolecular Structure? | Phase Stability? |
|------------|-------------------|--------------------------------|--------------------------------|------------------|
| Isomers    | yes               | no                             | no                             | s, l, g, sol.    |
| Polymorphs | yes               | yes                            | no                             | solids only      |

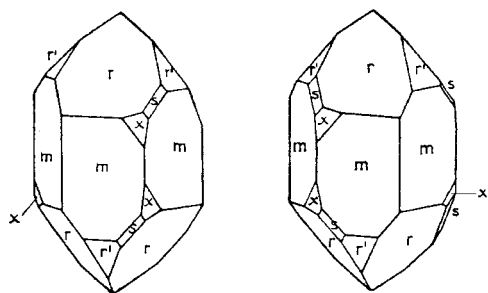


Figure 4. Left- and right-handed crystals of  $\alpha$ -quartz.

*persist after melting, vaporization, or dissolution, not because these processes have destroyed an intermolecular structure unique to solids, but because they have destroyed an infinitely extended intramolecular structure which is also unique to solids* ( $\delta$ ).

These considerations further suggest that polymorphism (an observable difference in crystal form) should be regarded as a molar phenomenon, whose underlying molecular rationale is ultimately traceable to one of the above forms of isomerism and that, as a consequence, those few cases which actually correspond to the classic rationale of this phenomenon, as personified by the case of rhombic versus monoclinic sulfur, should also be given a distinct name at the molecular level (Table 4). As mentioned in Lecture I, this logical necessity was already recognized by 19th-century textbooks, which usually employed the term "physical isomerism" to denote alternative intermolecular arrangements of otherwise identical discrete molecules, though I think that the term "packing isomerism" is more descriptive ( $\theta$ ).

In summary, we may now restate our conclusions as follows:

**Polymorphism:** At the molar level, a phenomenon in which two or more substances of identical composition exhibit different crystal forms in the solid state, these differences disappearing upon melting, vaporization, or dissolution. At the molecular level, these differences are all traceable to examples of topological, geometric, chiral, or packing isomerism or to examples of polymerism which fail to persist beyond the solid state.

In more general terms, we can state that there is no single unique molecular rationale for the phenomenon of allomorphy at the molar level, whether the allomorphs in question correspond to differences in state (as in our discussion of chemical versus physical change), to differences in crystal form (as in our discussion of polymorphism), or to differences in liquid crystal mesophases. In each instance, it is possible to find examples which correspond either to cases of polymerism or to cases of topological, geometric, chiral, or packing isomerism at the molecular level.

### Detection of Historically Outdated Definitions and Concepts

As our previous example has shown, a knowledge of the historical evolution of chemical concepts and models can often play a key role in disentangling illogical admixtures. The problems with most textbook definitions of polymorphism were the result of both a failure to correct outdated 19th-century assumptions about the molecular structure of solids and a failure to generalize the terminology of isomerism so

Table 4. A Summary of the Various Molecular Origins of Polymorphism

| Molar Level | Molecular Level     | Example                       |
|-------------|---------------------|-------------------------------|
| polymorphs  | topological isomers | $\alpha$ -tin vs $\beta$ -tin |
| polymorphs  | geometric isomers   | zinc blende vs wurtzite       |
| polymorphs  | chiral isomers      | left- vs right-handed quartz  |
| polymorphs  | packing isomers     | rhombic vs monoclinic $S_8$   |

as to subsume not only traditional finite molecular structures, but infinitely extended framework, layer, and chain structures as well. In this section we will analyze an even more blatant example of how a failure to correct outdated ideas can lead to the generation of illogical and self-contradictory definitions, this time involving the terms "atom", "molecule", and "element"—three concepts which lie at the very core of chemistry.

Even the most cursory survey of chemistry texts rapidly reveals that all of them adopt, either explicitly or implicitly, the hierarchical arrangement given in Figure 6 when discussing the composition/structure dimension of chemistry. Substances are made of molecules; molecules, in turn, are made of atoms; atoms are made of electrons and nuclei; and nuclei are made of protons and neutrons. We talk about *diatomic* and *polyatomic* molecules and about characterizing individual molecules in terms of the kind, number, and arrangement of their component atoms. You may recall that this was precisely the terminology that I used in Lecture I when defining molecular composition and structure. The relation between molecule and atom assumed by this hierarchy is in fact the classic 19th-century relationship introduced by Cannizzaro in 1858. However, it has been known for nearly a century that this relation is incorrect and does not properly merge with either the molar or the electrical levels of chemical discourse.

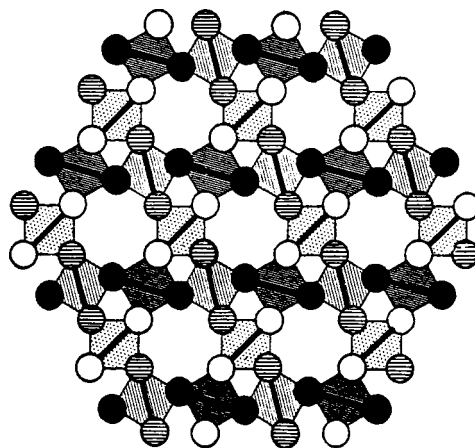


Figure 5. The structure of  $\alpha$ -quartz. The triangular channels are due to helices of tetrahedral  $\text{SiO}_{4/2}$  units that repeat every four tetrahedra. In the left- versus the right-handed forms of  $\alpha$ -quartz these helices spiral in opposite directions and thus account for the observed differences in optical activity.

At the molar/molecular interface, we are now aware of substances that are composed of discrete atoms rather than polyatomic molecules. These include, of course, the noble gases, and, if we divest ourselves of the parochialism that STP is somehow the natural state of things, rather than just an arbitrary reference state, it also includes most metals in the gas phase. At the electrical/molecular interface, we have known, almost since the turn of the century, that the particular electronic arrangement characteristic of isolated, neutral atoms is not preserved as such when atoms unite with one another to form molecules. An atom, according to the electrical theory of matter, corresponds to an isolated, non-interacting unit composed of a single nucleus and sufficient electrons to give the overall structure a zero net charge. When these atoms form ions or interact to form molecules, the number and/or the specific structural arrangement of these electrons is destroyed. Indeed, this electronic rearrangement is the very essence of chemical change, and it follows as a necessary corollary of this fact that neutral atoms cannot serve as structural units within polyatomic molecules and ions. As Mulliken and other proponents of molecular orbital theory have repeatedly emphasized over the last 60 years, molecules are made of nuclei and electrons and not of neutral atoms.

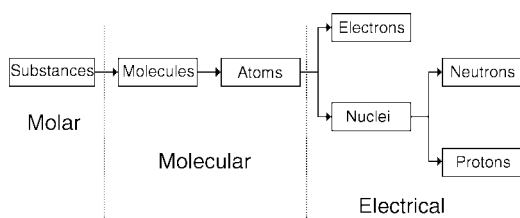


Figure 6. The normal textbook version of chemistry's composition/structure hierarchy.

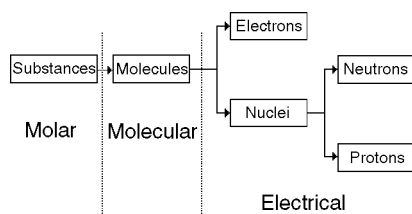


Figure 7. A corrected composition/structure hierarchy.

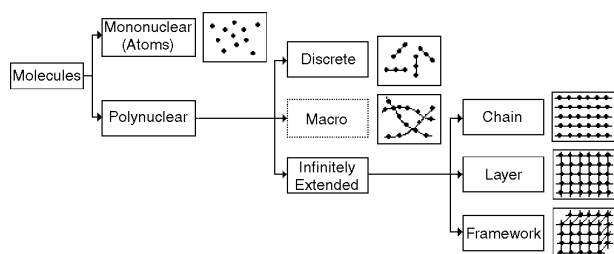


Figure 8. A modern structural classification of molecules.

These considerations suggest two important conclusions:

1. We should drop the use of such terms as diatomic, polyatomic, etc. and instead talk about dinuclear and polynuclear molecules. Likewise, we should talk about characterizing molecular composition and structure in terms of the kind, number, and arrangement of the component nuclei rather than the component atoms.
2. We should subsume isolated neutral atoms under the rubric of mononuclear molecules. In other words, the term molecule should be divorced from the late 19th-century requirement that it must of necessity be polynuclear and instead should be used as a general term for any neutral, kinetically independent, submicroscopic unit.

Adoption of these suggestions leads to the revised hierarchy shown in Figure 7, in which the term molecule now subsumes any of the following six classes: mononuclear molecules or atoms, discrete polynuclear molecules, discrete macromolecules, infinitely extended framework molecules, infinitely extended layer molecules, and infinitely extended chain molecules (Fig. 8).

Closely related to this problem is the pervasive use of the term "element" as both a synonym for the term "simple substance" at the molar level and as a synonym for the term "atom" at the molecular level. However, if we critically analyze how we use this term, we quickly conclude that it belongs to neither the molar nor the molecular level of discourse but to the electrical level. All chemists would agree that the element copper is present not only in copper metal, but in copper dichloride; in an isolated, neutral, gaseous copper atom; in a  $\text{Cu}^{2+}$  ion; and in a bare  $\text{Cu}^{29+}$  nucleus found in the core of a high-temperature star. All of these examples correspond to very different electronic environments, and the only feature they have in common which would justify the assertion that the element copper is present in all cases is the presence of the copper nucleus. In other words, neither metallic copper nor the neutral copper atom correspond to the element copper, any more than does copper dichloride, though all three contain the element copper. This admission leads, in turn, to the logical conclusion that the term "element" is in fact a descriptor for a particular kind of nucleus, or more accurately, for a particular "class" of nuclei, all of which have the same atomic number. Hence the formal definition:

*Element: A class of nuclei, all of which have the same atomic number.*

The caveat in this definition is, of course, necessitated by the existence of isotopes. The introduction of this concept by British radiochemist Frederick Soddy in 1913 led to an intensive debate in the chemical literature of the period among Soddy, Kasimir Fajans, and Fritz Paneth as to how the term element should be redefined in light of our new knowledge of the electrical structure of matter, in which Soddy's proposed terminology proved the ultimate victor (9–11). Each box of the periodic table corresponds to a single element or class of nuclei having identical atomic numbers. Since the individual varieties corresponding to each class all occupy the same location in the table, Soddy suggested the term isotope (from the Greek for "equal place") to describe them (12). Thus, our final hierarchy is as follows: substances are made of molecules; molecules are made of electrons and

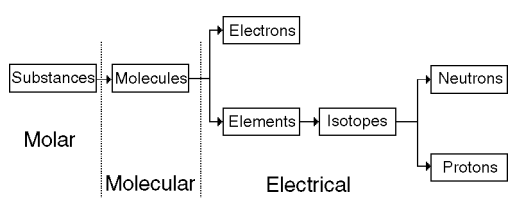


Figure 9. A composition/structure hierarchy incorporating the concept of "element."

elements, elements are resolvable into individual isotopes, and isotopes are made of protons and neutrons (Fig. 9). Contrary to Lavoisier, isotopes rather than elements now represent the final stage of chemical (i.e., non-nuclear) analysis (13).

Just to make life even more complex, it is worth noting that chemists customarily introduce at least one additional stage into this hierarchy at the electrical level via the time-honored practice of distinguishing between valence electrons and core electrons (Fig. 10). *Nevertheless, however we slice things, we cannot evade the conclusion that the isolated neutral atom no longer occupies a fundamental position in the structural hierarchy of modern chemistry, but is instead but one of many possible products—albeit the simplest—which result from the interaction of atomic cores and valence electrons or, at a more fundamental level, from the interaction of elements and electrons. The specific structural entity we now identify with the term atom does not persist within ions and molecules. What does persist are the electrons and nuclei.* The fact that most introductory textbooks continue to use what are, in essence, residual 19th-century definitions of the concepts of atom, element and molecule, while simultaneously describing modern 20th-

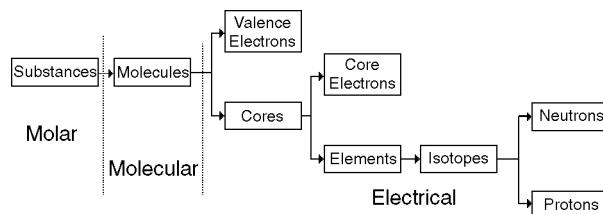


Figure 10. A composition/structure hierarchy incorporating the concept of core and valence shell.

century developments, is an apparent contradiction made possible only by the pervasive compartmentalization of topics characteristic of most of these textbooks (14).

Before leaving this subject, it should perhaps be emphasized that the assertions made in this section about the status of neutral atoms in the current composition/structure hierarchy of chemistry are not meant to imply that atoms are unimportant in modern chemistry. As the simplest possible mononuclear molecules, they display simple and easily rationalized periodic trends for such properties as their ionization potentials, electron affinities, electronegativities, radii, polarizabilities, and characteristic X-ray absorption frequencies. Much of introductory chemistry can be viewed as an attempt to establish correlations between these simple atomic properties and the more complex properties of polynuclear molecules and infinitely extended solids. However, this use of neutral atoms as reference standards in establishing property-composition correlations with more complex systems is quite independent of their status (or rather nonstatus) as fundamental units in the current composition/structure hierarchy of modern chemistry.

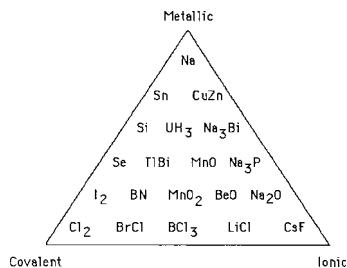


Figure 11. Jolly's 1984 bond-type triangle.

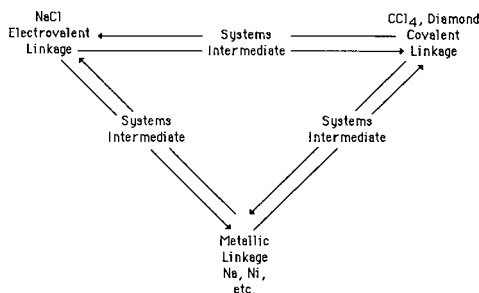


Figure 12. Fernelius and Robey's 1935 bond-type triangle.

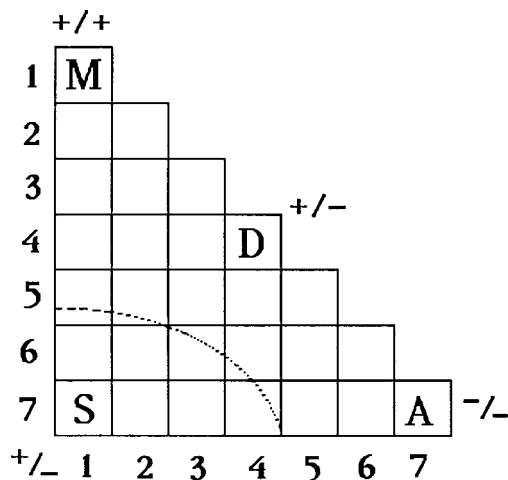


Figure 13. Grimm's 1928 "Dreieckschema" produced by constructing intra- and inter-row binary combination matrices for the elements in the periodic table. Each square represents a binary compound formed from the elements having the group numbers listed along the vertical and horizontal edges. The letters indicate the general character of the resulting compounds: A = Atommoleküle, D = Diamantartige Stoffe, M = Metalle, and S = Salze.

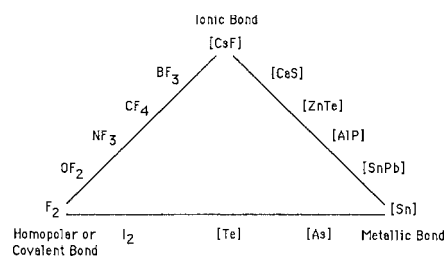


Figure 14. van Arkel's 1941 bond-type triangle. Formulas in brackets indicate infinitely extended solids.

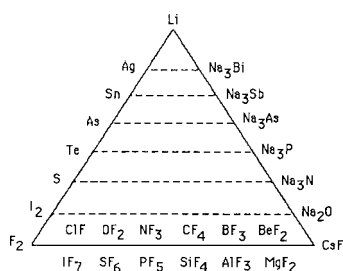


Figure 15. Ketelaar's 1947 bond-type triangle.

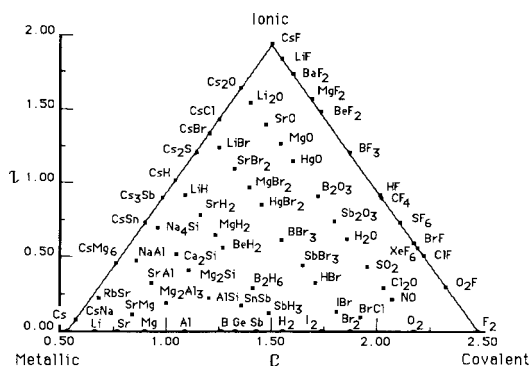


Figure 16. A quantified bond-type triangle.

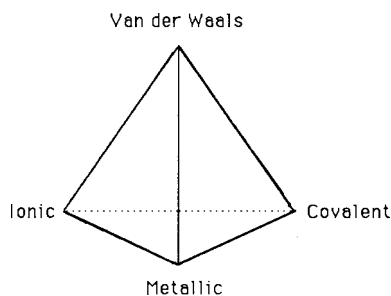


Figure 17. Laing's bond-type tetrahedron.

## Resolution of Contradictory Claims

As a final example of how our logic diagram can be used to clarify our use of chemical concepts and models, I would like to briefly illustrate how it may be used to resolve a debate in the current chemical education literature over the best way of representing the concept of intermediate bond types.

Most introductory textbooks discuss the idea of three separate mechanisms for chemical bonding: the ionic bond, based on electron transfer; the covalent bond, based on the sharing of electron pairs; and the metallic bond, based on the sharing of a delocalized electron gas. More advanced texts further point out that these three bonding mechanisms correspond to idealized limiting-cases, and that most chemical substances actually contain bonds that are intermediate in character. Often this concept is illustrated by means of a triangular diagram, similar to the example in Figure 11, which is taken from the 1984 edition of William Jolly's text, *Modern Inorganic Chemistry* (15). I have been able to trace these diagrams back to a 1935 article in the *Journal of Chemical Education* by the American chemists Conard Fernelius and Richard Robey (Fig. 12) and, in a more preliminary form (Fig. 13), to a 1928 article by the German chemist Hans Georg Grimm (16, 17). However, the version of the diagram (Fig. 14) which appears in most textbooks is actually based on a 1941 text by the Dutch chemist Anton Eduard van Arkel (18) or, even more commonly, on a 1947 text (19) by van Arkel's colleague, the Dutch chemist Jan Arnold Albert Ketelaar (Fig. 15). For this reason these diagrams are often referred to in the chemical literature as van Arkel–Ketelaar triangles, though this is certainly unfair with respect to the earlier contributions of Fernelius and Grimm.

In all of these examples, the placement of the example compounds on the triangle was qualitative and, as such, was a function of each author's chemical intuition. However, more recently, several proposals (20–22) have been made for quantifying these diagrams, one of the simplest involving a plot of the difference in the electronegativities of the two bonded atoms versus their average electronegativity (Fig. 16):

$$\text{Ionicity} = I = \Delta EN = (EN_B - EN_A) \quad (1)$$

$$\text{Covalency} = C = EN_{av} = (EN_A + EN_B)/2 \quad (2)$$

The first of these parameters serves as a measure of the asymmetry or ionicity of the A–B bond and the second as a measure of its localization or covalency.

But even as these apparent advances were being made, a number of articles began to appear in the educational literature criticizing the use of such diagrams and proposing instead alternative approaches to this subject. Thus, in an article which appeared in the November 1993 issue of *Education in Chemistry*, the South African chemist Michael Laing criticized the traditional Ketelaar triangle "for having misled generations of students into wrongly associating a low melting point with covalent bonding within the solid, when in fact the reverse is true. It is the weak van der Waals forces that must be associated with low melting points, while a network of covalent bonds leads to a high melting point" (23). To remedy this defect, Laing proposed replacing the Ketelaar triangle with a "bonding tetrahedron" which explicitly takes van der Waals attractions into account as a fourth type of bonding interaction (Fig. 17). Through a consideration of melting points, conductivities of the solid and liquid states, bond distances, and coordination numbers, Laing then pro-

ceeded to discuss the qualitative placement of several binary compounds and simple substances on his diagram.

Two months later, in the January 1994 issue of the *Journal of Chemical Education*, the British chemist Peter Nelson published yet another paper criticizing the traditional classification of substances in terms of bond type (24). In this article Nelson argued that "bond type" was a purely theoretical concept which could not be directly measured, and which lacked a precise theoretical definition (as reflected by a lack of agreement as to how it should be quantified). As an alternative, he proposed a triangular diagram which classified substances in terms of the magnitude and nature (i.e., electronic versus ionic) of their bulk conductivities (Fig. 18). This replaced the traditional classes of covalent, ionic, and metallic substances with insulators, electrolytes, and metals, respectively, and included semiconductors, semi-electrolytes, and mixed-conductors as intermediate cases.

The key to unraveling these apparently conflicting claims lies in the recognition that the terms ionic, covalent, and metallic represent a classification of bonds at the electrical level. The quantified van Arkel triangle, shown in Figure 16, is designed to graphically illustrate the gradual transition between these various limiting-case models at the electrical level and does so in terms of atomic electronegativities, which are also defined at the electrical level. Though most presentations of the triangle have used examples of binary compounds and simple substances to illustrate these transitions, the triangle really refers only to the A-B bonds present in these materials. It has nothing to say about the A-A and B-B interactions which are also present and hence nothing to say about either the molecular structures of these example compounds or their bulk molar properties, such as melting points, boiling points, electrical conductivities, or solubilities. To avoid potential misunderstandings and misuse of the diagram, it would probably be best to discontinue the practice of using actual compounds as examples and instead simply indicate the nature of the two interacting atoms in the corresponding bond (Fig. 19).

The diagram proposed by Nelson, on the other hand, corresponds to a classification of pure substances at the molar level. In keeping with this premise, he has recently suggested that the diagram might be quantified by plotting a temperature-weighted function of the bulk ionic and bulk electronic conductivities of a material, both of which are capable of being defined and measured at the molar level,

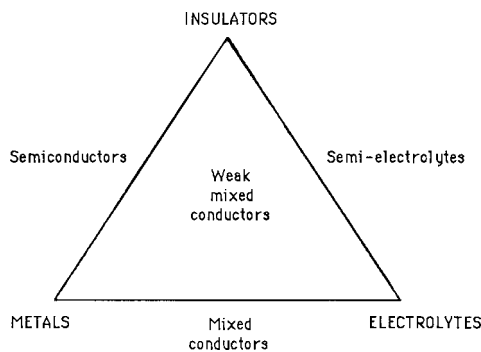


Figure 18. Nelson's alternative classification triangle based on bulk conductivity mechanisms.

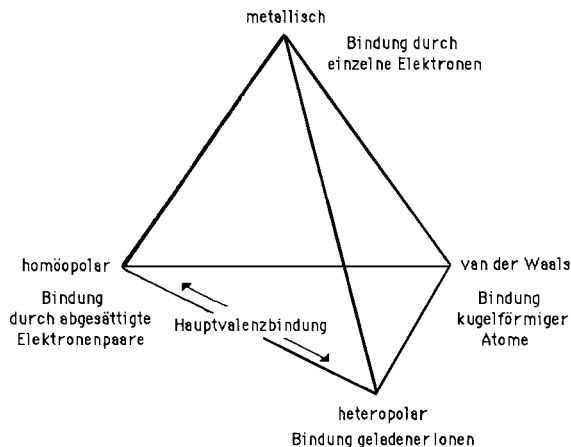


Figure 20. Dehlinger's 1934 drawing of Grimm's bond-type tetrahedron.

though the necessary data are still lacking for many substances (25). In any case, the bottom line is that the terms ionic, covalent, and metallic should be eliminated from the molar level of discourse. They describe bonds at the electrical level and not substances at the molar level, where they should be replaced instead by a terminology similar to that proposed by Nelson.

The diagram proposed by Laing is more problematic in nature, in part because of the absence of any quantitative coordinates and, in part because it appears to be simultaneously intermixing two separate classification criteria. Indeed, a much more precise version of the identical diagram was proposed by the German chemist Hans Georg Grimm nearly 70 years ago. This is shown in Figure 20 as a three-dimensional tetrahedron, taken from a 1934 paper by Ulrich Dehlinger, and in Figure 21 as a two-dimensional projection of the tetrahedron, taken from a paper published by Grimm the same year, but redrawn for greater clarity using corrected and updated examples (26, 27).

As can be seen, Grimm attempted to simultaneously classify binary compounds and simple substances in terms of both their structure type and bond type. Three of the vertices of the tetrahedron correspond to infinitely extended framework structures containing ionic ( $i$  = Ionenbindung), covalent ( $a$  = Atombindung), and metallic ( $m$  = metallische

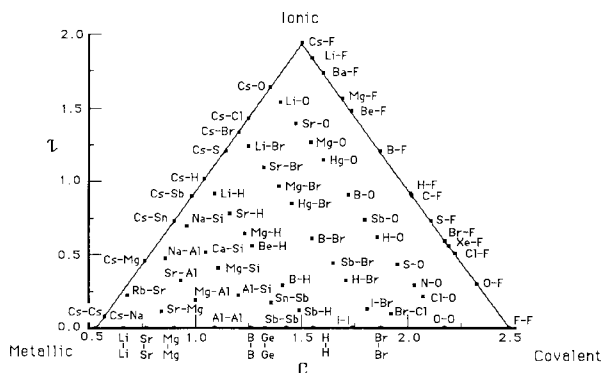


Figure 19. A labeled version of Figure 16 showing bonds rather than compounds and simple substances.



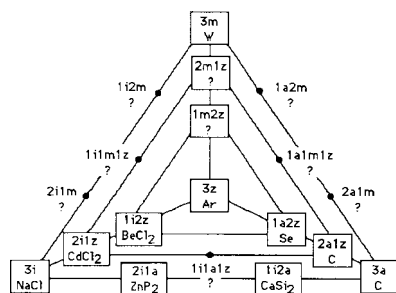


Figure 21. Grimm's two-dimensional projection of his 1934 bond-type tetrahedron. Redrawn using corrected and updated examples (i = Ionenbindung, a = Atombindung, m = metallische Bindung, and z = zwischenmolekulare Kräfte).

Bindung) bonds, respectively, whereas the fourth vertex corresponds to discrete atoms and molecules held together in the crystal lattice by means of weak van der Waals interactions (z = zwischenmolekulare Kräfte). In each of these cases, the particular type of bonding network present in the crystal is envisioned as extending indefinitely in three dimensions, whence the use of the symbols, 3i, 3a, 3m and 3z. Thus, sodium chloride corresponds to an ionically bonded (3i) framework structure, diamond to a covalently bonded (3a) framework structure, tungsten to a metallicly bonded (3m) framework structure, and argon to a (3z) discrete molecular structure. (Table 5, first section.)

At one-third of the distance along the edges connecting the (3z) van der Waals vertex with the other vertices, one finds infinitely extended layer structures in which one dimension corresponds to a van der Waals interaction between the layers and the other two dimensions correspond to one of the other three bond types. Thus, graphite corresponds to a covalently bonded (2a,1z) layer structure and cadmium dichloride to an ionically bonded (2i,1z) layer structure (Table 5, second section). At two-thirds of the distance along these edges, one encounters infinitely extended chain structures in which two of the dimensions correspond to van der Waals

**Table 5. Examples of Simple Substances and Binary Compounds Corresponding to the Various Classes Found in Grimm's Bonding Tetrahedron as Shown in Figure 21**

| Example              | Structure Class              | C/N Formula                               | Grimm  |
|----------------------|------------------------------|---|--------|
| Sodium chloride      | ionic framework              | $\frac{1}{2}[\text{NaCl}]_{6/6}$          | 3i     |
| Diamond              | covalent framework           | $\frac{1}{2}[\text{C}_{4/4}]$             | 3a     |
| Tungsten             | metallic framework           | $\frac{1}{2}[\text{W}_{6/6}]$             | 3m     |
| Solid argon          | finite mononuclear molecules | $\frac{1}{2}[\text{Ar}_{12/12}]$          | 3z     |
| Graphite             | covalent layer               | $\frac{1}{2}[\text{C}_{2/2}]$             | 2a, 1z |
| Cadmium dichloride   | ionic layer                  | $\frac{1}{2}[\text{CdCl}_{4/2}]$          | 2i, 1z |
| Selenium             | covalent chain               | $\frac{1}{2}[\text{Se}_{2/2}]$            | 1a, 2z |
| Beryllium dichloride | ionic chain                  | $\frac{1}{2}[\text{BeCl}_{4/2}]$          | 1i, 2z |
| Calcium disilicide   | covalent layer anion         | $\frac{1}{2}\text{Ca}[\text{Si}_{2/2}]_2$ | 1i, 2a |
| Zinc diphosphide     | covalent chain anion         | $\frac{1}{2}\text{Zn}[\text{P}_{2/2}]_2$  | 2i, 1a |

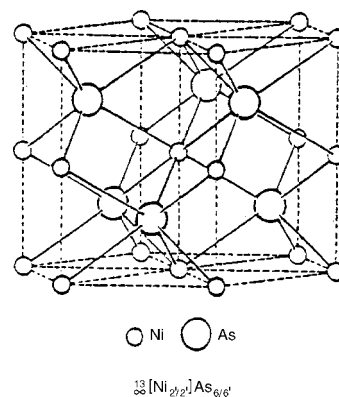
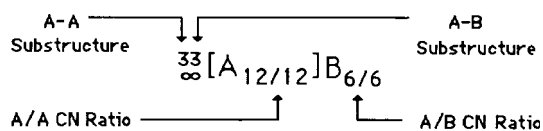


Figure 22. The structure of nickel arsenide.

interactions and the third to the nature of bonding within the chain itself. Thus, selenium corresponds to a covalently bonded (1a,2z) chain structure and beryllium dichloride to an ionically bonded (1i,2z) chain structure (Table 5, third section). The other edges of the triangle correspond to structures with mixed bonding. Thus, calcium polydisilicide, which contains infinitely extended, covalently bonded 3/3 silicon layer anions held together by calcium cations, corresponds to a (1i,2a) structure and is located two-thirds of the distance along the edge of the tetrahedron connecting the 3i and 3a vertices, whereas zinc polydiphosphide, which contains infinitely extended, covalently bonded 2/2 phosphorus chain anions held together by zinc cations, corresponds to a (2i,1a) structure and is located at one-third of the distance along the same edge (Table 5, fourth section).

Note that Grimm failed to provide examples for most of the points on the tetrahedron corresponding to structures containing infinite one- and two-dimensional metallic bonding arrays, though the so-called condensed cluster compounds studied in recent years by the German chemist Arndt Simon and others probably correspond to these cases, as do several more classic compounds, such as nickel arsenide (28). This latter substance would appear to contain infinitely extended nickel chains held together by weak, metallic bonding and cross-linked by means of idealized, ionic Ni-As bonds into an infinitely extended (2i,1m) framework structure (Fig. 22).

As appealing as Grimm's classification appears, it does not take long to uncover some fundamental limitations. Take, for example, the monoxides, mononitrides and monocarbides of the D- and F-block elements (Fig. 23), often referred to as so-called interstitial compounds (29). At first glance, these all appear to have a simple 6/6 infinitely extended (3i), ionic A-B framework structure like sodium chloride. However, their optical and electrical properties, the metal-metal distances in their structures, and their metallic appearance are all suggestive of the simultaneous existence of an infinitely extended (3m), metallic A-A bonding network, and it is not apparent where one would



EXAMPLES: UO, TiO, LaN, NbO, TaC, TiC, etc.

Figure 23. The structure of the so-called D- and F-block interstitial oxides, nitrides, and carbides.

locate the resulting (3i,3m) structures on Grimm's tetrahedron. A somewhat similar problem also arises with the nickel arsenide and condensed cluster structures mentioned earlier, as in all cases the A-B bonding appears not only to cross-link the metallic chains and layers, but also to reinforce the bonding within the chains and layers. Or take the case of calcium polydicarbide, which contains not only an infinitely extended 6/6 framework structure held together by ionic Ca-C bonds, but discrete, dinuclear  $C_2^{2-}$  anions held together by covalent C-C bonds (Fig. 24). Since the bonding tetrahedron explicitly indicates only infinitely extended bonding networks, it cannot represent the existence of the isolated covalent bond within the polydicarbide anion.

Though Laing's version of the tetrahedron lacks the precision of Grimm's diagram, he appears to be groping toward a similar classification. His point about the neglect of van der Waals interactions and their role in determining melting point is really a way of saying that melting point depends more on molecular structure type than on bond type. Thus the fact that magnesium oxide, diamond, and tungsten metal all have extremely high melting points has more to do with the fact that all three contain infinitely extended framework structures than it does with the fact that the first contains ionic bonds, the second contains covalent bonds, and third contains metallic bonds (Table 6). Likewise, the fact that both white tetraphosphorus and sulfur hexafluoride have low melting points (Table 7) has more to do with the fact that they are both composed of discrete molecules than with the fact that the first contains covalent bonds and the second contains relatively ionic bonds (30). The observation that most molar properties correlate with molecular structure rather than with bond type has been emphasized many times, most notably by Kossel in 1920, by Pauling in 1932, by Stillwell in 1936, and most recently by Lingafelter in 1993; yet as Laing emphasized, it is almost impossible to pick up an introductory textbook which does not claim that high melting points indicate ionic bonding and low melting points indicate covalent bonding (31-35).

It seems to me that the best way to eliminate this incorrect association is to completely remove the bond type criterion from the diagrams suggested by Laing and Grimm and to develop instead a purely structural classification at the molecular level of discourse. The result is shown in Figure 25 (36). As can be seen, we still have a tetrahedron, but the interpretation of the vertices and edges is very different from that found in the original Grimm-Laing diagram. In our case, each vertex corresponds to one of the four major classes of molecules mentioned in the previous sec-

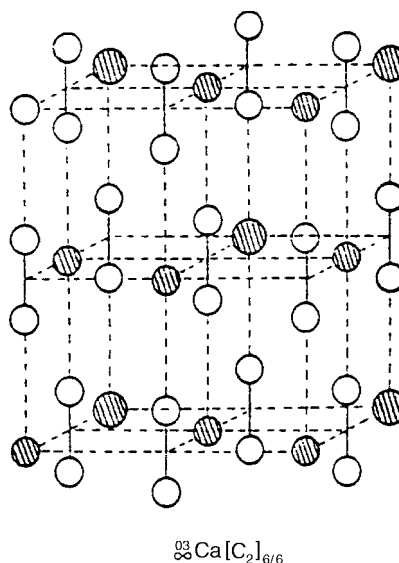


Figure 24. The structure of calcium polydicarbide.

tion. The  $\overset{\infty}{\infty}$  vertex corresponds to discrete molecules, including isolated atoms; the  $\overset{1}{\infty}$  vertex corresponds to infinitely extended chain structures; the  $\overset{2}{\infty}$  vertex corresponds to infinitely extended layer structures; and the  $\overset{3}{\infty}$  vertex corresponds to infinitely extended framework structures. No reference is made to the nature of the bonding which gives rise to these structures.

Thus, materials with high melting points, such as magnesium oxide, diamond, and tungsten, are all found at the  $\overset{3}{\infty}$  vertex by virtue of their common framework structures, irrespective of the fact that the first is held together by ionic bonds, the second by covalent bonds, and the third by metallic bonds.<sup>1</sup> Likewise, low-melting materials, such as white tetraphosphorus and sulfur hexafluoride, are all found at the  $\overset{0}{\infty}$  vertex by virtue of their discrete molecular structures, irrespective of the nature of their intramolecular bonds. The edges and faces of this tetrahedron now correspond to intermediate structures containing strong intermolecular attractions, such as hydrogen bonding (Fig. 26). Thus the H-

Table 6. Examples of Framework Structures with High Melting Points Corresponding to the Ionic, Covalent, and Metallic Bonding Extremes

| Substance       | Structure                         | Melting Point [°C] | Bonding  |
|-----------------|-----------------------------------|--------------------|----------|
| Magnesium oxide | $\overset{3}{\infty} [MgO_{6/6}]$ | 2802               | Ionic    |
| Diamond         | $\overset{3}{\infty} [C_{4/4}]$   | 3547               | Covalent |
| Tungsten        | $\overset{3}{\infty} [W_{6/6}]$   | 3407               | Metallic |

Table 7. Examples of Discrete Molecular Structures with Low Melting Points Corresponding to the Ionic and Covalent Bonding Extremes

| Substance           | Structure                    | Melting Point [°C] | Bonding  |
|---------------------|------------------------------|--------------------|----------|
| Sulfur hexafluoride | $\overset{0}{\infty} [SF_6]$ | -50.7              | Ionic    |
| White phosphorous   | $\overset{0}{\infty} [P_4]$  | 44.3               | Covalent |

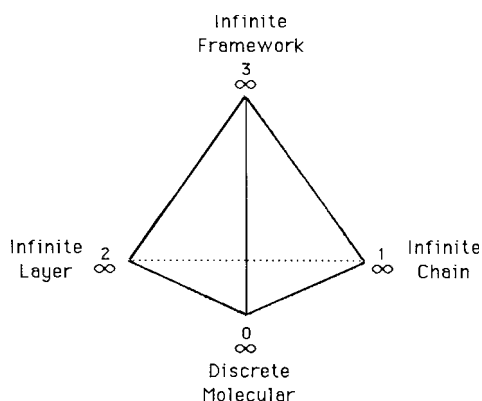


Figure 25. A tetrahedron for the structural classification of pure substances at the molecular level.

bonded framework structure of ice is found along the edge joining the  $\infty$  vertex with the  $\frac{3}{\infty}$  vertex; the H-bonded layer structure of boric acid is located along the edge joining the  $\infty$  vertex with the  $\frac{2}{\infty}$  vertex; aluminum trihydroxide, which contains an infinitely extended layer structure held together by strong interlayer H-bonds, lies along the edge joining the  $\frac{2}{\infty}$  vertex with the  $\frac{3}{\infty}$  vertex, etc.

These results reinforce the conclusion that we reached earlier with respect to Nelson's work. The terms ionic, covalent, and metallic should be eliminated, not only from the molar level of discourse, but from molecular level as well. They describe bonds at the electrical level and not substances at the molar level nor structures at the molecular level. Our analysis also leads to the further conclusion that we are not dealing with three competing versions of the same thing, but rather with three distinct diagrams, each of which refers to a separate level of chemical discourse: the quantified van Arkel triangle, which deals with the classification of bonds at the electrical level; the modified Grimm tetrahedron, which deals with the classification of structure at the molecular level; and the Nelson triangle, which deals with the electrical classification of substances at the molar level (Table 8).

These diagrams cannot be mutually interchanged because they each deal with a different subject and do so at very different levels of discourse. Thus, though I agree with Nelson's suggestion that it would be better in an introductory course to begin with a molar classification of chemical substances, similar to that in his proposed diagram, rather than with a more abstract bond classification, such as the van Arkel diagram, it is apparent that Nelson's diagram can only function as a supplement, rather than as an alternative, to the van Arkel triangle, since in a textbook chapter dealing with the nature of the chemical bond, one needs to use a diagram that deals directly with the bonds themselves, however theoretically abstract the parameters may be, rather than

Table 8. A Summary of the Three Diagrams

| Diagram                    | Subject           | Level      |
|----------------------------|-------------------|------------|
| van Arkel triangle         | Bond type         | Electrical |
| Modified Grimm tetrahedron | Structure         | Molecular  |
| Nelson triangle            | Bulk conductivity | Molar      |

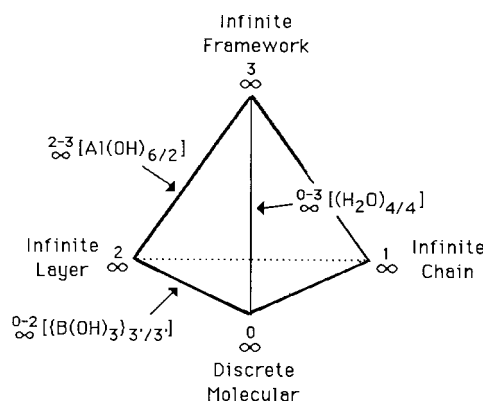


Figure 26. An elaboration of the structure-type tetrahedron in Figure 25 showing examples of intermediate, H-bonded structures along the edges.

with a diagram that deals with the molar electrical properties of pure substances.

This is not to say that these three diagrams cannot be interconnected. However, this interfacing requires the use of the two fundamental postulates given in Lecture I. These show that properties at one level of discourse are usually a function of several factors at the next lower level. Only by carefully selecting our examples so that all but one or two of these factors are held constant, is it possible to correlate one level with another using a two-dimensional diagram. Thus, the structure of binary compounds at the molecular level depends not only on the nature of their A–B bonds but on the ratio in which A and B are combined, and thus ultimately on the ratio of valence electrons to atomic cores or the VEC (valence electron concentration), as it is commonly called in the solid-state literature:

$$\text{Structure of } A_aB_b = f(EN_A, EN_B, \text{VEC}) \quad (3)$$

This is really another way of saying that structure at the molecular level depends on both the kind (as expressed by the EN values of the cores) and relative number (as expressed by the VEC value) of the component particles at the electrical level. If we suppress this second factor by plotting only compounds with identical VEC values, we then find that there is a correlation between molecular structure at level 2 and bond type at level 1 that can be displayed on the van Arkel dia-

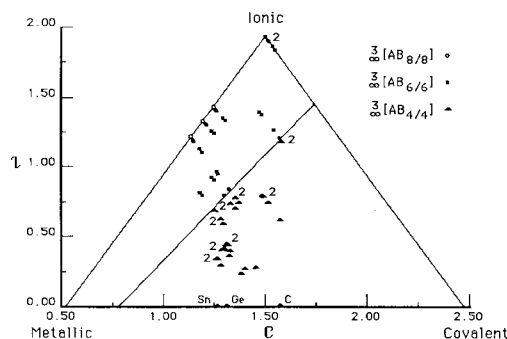


Figure 27. A structure-sorting map for 1:1 binary compounds and simple substances with a VEC = 4.

gram, and that is shown in Figure 27 for 1:1 AB compounds with VEC values of four.<sup>2</sup>

## Notes

1. Even after eliminating bond type, the correlation between structure type and melting point is not as simple as suggested here, since it also depends on bond strength. Thus, despite its infinitely extended framework structure, cesium metal has a low melting point because of the low bond energy per Cs–Cs pair.

2. See reference 20. Reference 21 provides examples of an incorrect mixing of compounds with variable VEC values on the same bond-type diagram, as well as an incorrect use of the diagram to maintain the idea that there are sharp boundaries separating substances containing metallic, covalent, and ionic bonds. Unfortunately, all of these misinterpretations are repeated in the recently published text: Bodner, G. M.; Rickard, L. H.; Spencer, J. N. *Chemistry: Structure and Dynamics*, Wiley: New York, NY, 1996; pp 184–189.

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