

Electronegativity and Bond Type: Predicting Bond Type

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Electronegativity, EN, and electronegativity difference, ΔEN , are used to explain many chemical observations such as acidity of solvents, mechanisms of chemical reaction, distribution of electrons, and polarity of bonds. Essentially all general chemistry textbooks during the past 30 years have indicated that the ΔEN between bonded atoms is an indication of whether compounds should be classified as ionic or covalent. Some authors use a ΔEN value of 1.7 (or a value between 1.5 and 2.0) to roughly divide these compounds by bond types. Others recognize the gradual variation from polar covalent to ionic bonding but do not provide numerical discrimination. Thus, there has been no general agreement on what, if any, value of ΔEN should be used to predict bond type. It is the purpose of this paper to show that ΔEN is an improper function for separating ionic from covalent bonding.

Background

Pauling recognized that bonds between unlike atoms in a compound typically have a greater bond energy than that of the average of the corresponding homoatomic bonds (1, p 100). From this he reasoned that there is added stability in heteroatomic bonds arising from an ionic component of energy due to coulombic attraction from partially and oppositely charged heteroatomic atoms. To quantitate these observations, he defined the term *electronegativity* as the power of an atom in a molecule to attract electrons. On the basis of this definition, Pauling then devised equations based on ΔEN to estimate bond energies between heteroatomic atoms (1, p 88). He also determined on the basis of dipole moment measurements that a ΔEN on the "Pauling" scale¹ of electronegativities of 1.7 indicated 50% ionicity.² Compounds with ΔEN less than this value could be described as having mostly covalent character and those with a greater value were said to be mostly ionic.

Since the publication of Pauling's description of bonding, ΔEN has been used to estimate relative ionic contributions in heteroatomic bonds. Nevertheless, it is widely recognized that this algorithm provides only an imprecise guide to bonding character. General chemistry textbooks can be separated into two categories by how they describe this imprecision. The first group of texts provides a numerical value that (roughly) divides ionic from covalent bonding; these often follow the arguments of Pauling by stating that a ΔEN of 1.7 (or some value between 1.5 and 2.0) can be used to make an approxi-

mate division (2). The second group of textbooks states that it is improper to designate any specific dividing line, but that ΔEN values can serve as a rough guide for evaluating bond character (3).

Interatomic bonding is often characterized by one of three bonding models: ionic, covalent, or metallic. Classification of compounds into one of these is based on various physical properties including electrical conductivity of the solid, liquid, and solution states; luster; solubility in polar solvents; and crystalline structure. Many compounds can be reasonably categorized as one of these three types, although it is generally recognized that most heteroatomic bonds exhibit a mixture of these ideal bond types (4).

In his several editions of *Structural Inorganic Chemistry* (5), A. F. Wells characterized compounds on the basis of their structural and physical properties. Because the physical properties of many compounds suggest a mixed bond character, Wells generally chose to describe compounds geometrically (5, p 64). He avoided use of values of EN or especially ΔEN to describe bond type (6). Nevertheless, throughout his book he described many compounds that exhibit primarily only one of each of the three "ideal" bonding types, using terms such as "ionic", "essentially covalent", "metallic bonds", "molecular", etc. By selecting only binary compounds formed by representative elements that exhibit primarily one of the three classes of bonding, a data set containing each of the three "ideal" compound types was compiled. This set consists of 312 binary compounds, of which 164 were described as covalent, 94 as ionic, and 54 as metallic.³ Using this data set of well-categorized compounds, it has been possible to compare the three bonding types with various functions of EN.

The Problem with Electronegativity Differences

Because the ΔEN value for two bonded atoms converts the two EN terms into only one difference value, roughly *half of the information inherent in the two electronegativity values is lost with the difference function ΔEN* . To retain all of the information inherent in the two initial values, a second independent variable must be included. Since ΔEN is a difference function, the sum function that averages electronegativities is an obvious choice for this.

Dozens of scales of electronegativity have been proposed, some of which appear to be superior to the one described by

Pauling (7). However, because Pauling's scale is one of the most widely recognized scales, this one, as updated by Allred (8), was selected here for evaluation of bond type. Plotting ΔEN vs average EN for the 312 binary compounds of representative elements of known bonding type produces an isosceles triangle (Fig. 1). Such a diagram has been used intermittently for several decades to classify compounds according to their relative extent of covalent, ionic, and metallic bonding character (9, 10), and some authors have used it to demonstrate the gradual transition in bonding character between poles of "pure" bonding character (11). Metallic compounds (indicated by an M in the figure) are found in the lower left region (low average and low difference in electronegativity). Covalent compounds (C in the figure) occur in the lower right (large average and low difference in electronegativity), and ionic compounds (I in the figure) are found in the upper portion (large ΔEN).

The reason that simple ΔEN fails to adequately separate ionic from covalent compounds becomes clear. Collapsing the average EN data in the two-dimensional graph onto the vertical axis would be equivalent to using only the ΔEN function in a one-dimensional scheme. As can be seen in Figure 1, the line demarcating a boundary between ionic and covalent compounds lies at an angle to the axes, and does not correspond with any unique ΔEN value. Therefore, *no specific value of the function of ΔEN properly separates ionic from covalent compounds*. Authors of general chemistry texts unwittingly produce ambiguity whenever they attempt to define a cutoff between ionic and covalent compounds using any particular ΔEN value (or range of values).

The ΔEN demarcation value of 1.7 improperly assigns a bond type to many ionic and covalent compounds. Analysis of the data shows that this cutoff produces a 7% error in which primarily covalent compounds such as BF_3 , GeF_2 , HF, PF_3 , P_2F_4 , SiF_4 , Si_2F_6 , SnF_2 , SnF_4 , and TeF_4 would be misclassified as ionic. A huge 32% error occurs when predicting ionic character. Primarily ionic compounds such as GeO_2 , AlN , Be_3N_2 , Cd_3N_2 , GaN , Te_3N_4 , InN , Zn_3N_2 , MgBr_2 , CaS , Li_2S , SrS , Al_4C_3 , BaC_2 , Be_2C , CaC_2 , SrC_2 , BaH_2 , CaH_2 , CsH , KH , LiH , MgH_2 , NaH , RbH , and SrH_2 would be misclassified as covalent using this ΔEN demarcation. While it is clear that most of these compounds contain the mixed bond type expected along the boundary region, this does not alter the fact that their physical characteristics more properly describe them as having a different principal bond type. The overall error in identification of bond type using this ΔEN cutoff of 1.7 is 16% of the 258 ionic and covalent compounds. A similar problem would occur for any ΔEN cutoff value, since adoption of any ΔEN cutoff value *assumes* that ΔEN is the proper discriminator between ionic and covalent bonding. In addition, any other scale of electronegativity would produce comparable misclassification of bond type.⁴ With this amount of error in classifying compounds using ΔEN values, it is apparent why textbook authors need to include a caveat stating that no specific value of ΔEN can be used to differentiate between ionic and covalent bonding.

The two-dimensional graph of difference vs average electronegativity (Fig. 1) is instructive on other counts. It is clear that it is important to preserve the information contained in the individual electronegativities of bonded elements, rather than to rely on a function that converts two values of EN into

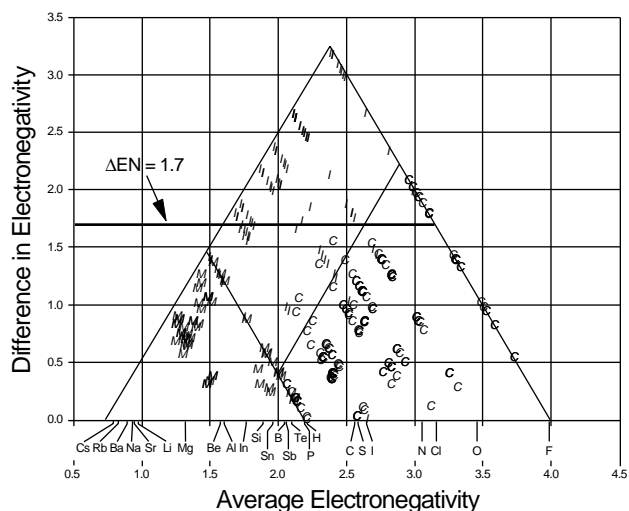


Figure 1. The vertical axis indicates differences in electronegativity and the horizontal axis gives average electronegativity for binary compounds of representative elements. Symbols locate several elements as well as ionic (I), covalent (C), and metallic (M) binary compounds. Lines divide regions of like bond character. The heavy horizontal line shows that the conventional cutoff value for a difference in electronegativity of 1.7 leaves many compounds incorrectly categorized.

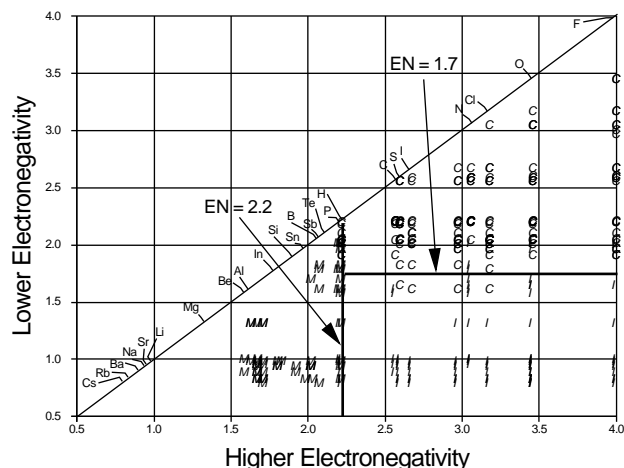


Figure 2. The vertical axis indicates lower electronegativity and the horizontal axis shows higher electronegativity for binary compounds of representative elements. Symbols locate several elements as well as ionic (I), covalent (C), and metallic (M) binary compounds. The dividing lines separating tripartite regions parallel the axes and successfully separate bonding types.

one difference term. It is also apparent that *metallic bonding can and should be included whenever comparing electronegativity values and bonding characteristics*. Additionally, it appears that the boundary lines separating the three bond types, although lying at a slanted angle to the selected axes, lie parallel to the sides of the isosceles triangle. This indicates that a change in axial coordinates could normalize this graph—and could perhaps provide additional insight into bond character.

Unfunctionalized Electronegativity Terms Define Bond Type

Changing the coordinates from differences and averages of EN to the unfunctionalized EN terms themselves (12) successfully normalizes the graphical presentation, as shown in Figure 2. Binary compounds are positioned on this graph by locating the value of the element of lower EN along the ordinate and the value of the element of higher EN along the abscissa. It can be seen with this axial system that the boundaries between the three types of compounds are now parallel to these axes. This indicates that this is, for some reason, the "natural" axial system for viewing the three bond types for binary compounds.

Without exception, compounds classified as metallic occur when the value of the element of higher EN has a value less than about 2.2.⁵ Whenever the value of the element of higher EN is greater than this, the element of lower EN governs bonding type. In these cases if the lower EN value is less than about 1.7, a compound is usually found to be ionic, whereas if the value is greater than 1.7 a compound is typically classified as covalent.

It is interesting to compare the ability to predict bonding type using both the difference function, ΔEN , as was done previously with $\Delta EN = 1.7$, and using these unfunctionalized terms. With the unfunctionalized EN values, there is only a 2% error in predicting covalent compounds and a 6% error for ionic compounds—and also now a 0% error in predicting metallic compounds. For both covalent and ionic compounds the unfunctionalized terms produce only a 4% overall error, far superior to the 16% error found when using the difference function. From this graphical analysis it is clear that a two-dimensional comparison using unfunctionalized electronegativity values provides discrimination far superior to that obtained using a difference function.

The two-dimensional graph also indicates that EN may provide a simple diagram for relating bonding characteristics in the three different classes of compounds. Although Pauling's definition of EN provided unitless quantities, more recent definitions state that EN is an energy concept. A most useful definition describes EN in terms of the average energy of the valence shell electrons (13). Following this definition, these results imply that *the average absolute energies (electronegativities) of valence electrons rather than differences in the energies (electronegativities) of bonded atoms determine bond type*. This is most apparent with the metallic compounds. Elements with low EN have valence electrons that are only loosely bound. Thus, when both elements in a binary compound have an EN value less than 2.2 (which corresponds to an energy of about 13.5 eV), their electrons are largely delocalized throughout the structure, and the compound has properties characteristic of a metal. However, if at least one of the elements has an EN value greater than this amount the valence electrons fall into a localized energy well. In this case if the element of lower EN has an EN less than about 1.7 (corresponding to an energy of about 9.5 eV) it loses its valence electron(s) to the element of higher EN and forms a cation in an ionic compound. When electronegativities of both elements are large, overlap and hybridization of their valence orbitals occur with the formation of a covalent compound (14).

Extension Using Transition Metals

It would be satisfying to independently confirm that the unfunctionalized EN values provide a means of separating bonding types. To this end a new set of compounds of known bond type was determined using binary compounds that contain at least one transition metal or inner transition metal atom (5). Positions of 327 of these compounds were plotted in a fashion analogous to that for compounds of the representative elements in Figure 2. Again, nearly all metallic compounds had values for the element of higher EN below the same cutoff previously determined for compounds of the representative elements.⁶ It came as no surprise that binary compounds involving transition metals with low EN (ionization energies) are classified as metals. However, unlike the successful separation of ionic and covalent compounds that was found for the representative elements, ionic and covalent compounds of transition metals were completely overlapped.

The reason for the overlap of ionic and covalent bonding is undoubtedly linked to the fact that many elements, particularly transition metals, characteristically exhibit multiple oxidation states, and different oxidation states can significantly alter the electronegativity of an element. For example, molybdenum(II) has an electronegativity of 2.16, whereas molybdenum(VI) has a value of 2.35 (8). Since transition metals can exhibit different oxidation states when bonded to the same element, separation using only a simple EN value for each of two bonded atoms and ignoring oxidation states will necessarily be inadequate. For example, the pairs of compounds $TiBr_2$ and $TiBr_4$, TiI_2 and TiI_4 , TcO_2 and Tc_2O_7 , RuO_2 and RuO_4 , and OsO_2 and OsO_4 are pairs of ionic and covalent congeners, respectively. Compounds of representative elements with different oxidation states such as $TiCl$ and $TiCl_3$ also show this dual character. Although their bonding character is different, these pairs would show no graphical separation from one another using only single-valued EN terms that are independent of oxidation state. For this reason, several authors have employed two-valued EN terms (see 15) that depend on valence states.

Another reason why the bonding type for compounds of transition metals is ill defined on the basis of EN alone is that transition metals have partially filled d orbitals available. These orbitals provide opportunity not only for coordinate-covalent bonding from a ligand but also for back-bonding from the metal to the ligand. Such mixed bonding confounds the simple description of covalent and ionic character. This exemplifies the inadequacy of using simple electronegativity values alone to predict ionic or covalent bonding character for compounds of the transition metals.

Although simple atomic EN values alone can be useful in predicting bond type in many compounds, other factors should also be considered. Pauling stated that "The properties of a compound depend on two main factors, the nature of the bonds between the atoms, and the nature of the atomic arrangement" (16). While atomic EN values can be used as an aid for determining bond type, these values alone are inadequate because they are modified by interatomic structural interactions (17). To predict bond character properly, it seems apparent that along with EN values of isolated atoms, some function of structural parameters must be taken into account. Recent work in my laboratory reveals a good inverse

correlation between coordination number and oxidation number. While oxidation or valence numbers are not measurable, the structurally determinable coordination numbers are measurable and could be incorporated when attempting to predict bond type.

Recommendations for Using Electronegativities in General Chemistry

The concept of electronegativity is a valuable tool for explaining many of the trends observed in chemistry. However, like all generalizations, it has its limitations. When this concept is presented in general chemistry, not only the advantages of the generalization but its shortcomings should be made clear.

First, although differences in electronegativities are helpful for describing certain concepts such as bond polarity and acidity, it is the absolute values of electronegativity and not differences in these values that are most useful for predicting bond type.

Second, the value of electronegativity of the element of higher electronegativity in binary compounds determines whether the compound will be metallic. If a compound is not metallic, the electronegativity of the element of lower electronegativity determines whether the compound will exhibit primarily ionic or covalent character if that element is a representative element. If the element of lower electronegativity is a transition metal the bond character is not predictable using electronegativities alone.

Third, electronegativity can be used as a guide for determining bond type, but for all except homoatomic bonds, bonding is a mixture of the three ideal bond types.

Supplemental Material

Supplemental material for this article is available in this issue of *JCE Online*.

Notes

1. Dozens of scales of electronegativity have been proposed, and some appear to be superior to that described by Pauling (7, 19). Various physical parameters have been used to develop these scales, including bond energies, ionization energy, electron affinity, atomic radius, polarizability, number of valence electrons, and pseudopotentials. However, because Pauling's scale is one of the most widely recognized scales of electronegativity, this scale, based on bond energies, is used in this paper.

2. The use of dipole moments to determine ionicity has been seriously questioned. Several authors have noted that dipole moments are a molecular property, whereas bond ionicity is a property of individual bonds. Dipole moments include not only the dipolar nature of bonds but also contributions from nonbonding electrons (18).

3. There were 58 covalent congeners, which used the same two elements but had different stoichiometries, 13 ionic congeners, and 4 metallic congeners. Thus, there were a total of 106 different covalent pairs of atoms, 81 ionic pairs and 50 metallic pairs.

4. Using Allen's scale, the errors are comparable and found to be 6%, 34% and 16%, respectively.

5. Because of the similarity in values of electronegativity in the Pauling scale (2.19 for phosphorus and 2.20 for hydrogen), a value of 2.195 was used to separate metallic compounds from others. Using other scales of electronegativity, such precision was typically unnecessary.

6. Electronegativity values in the Pauling scale as updated by Allred depend explicitly on oxidation state, but values for all desired oxidation states are not available for this scale. Therefore Allen's scale, which uses electronegativity values that are independent of oxidation state, was chosen for this analysis (personal communication with Leland C. Allen, Aug 14, 1997).

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