

Periodic Compounds: Syntheses at High Pressures and Temperatures

Abstract. A new class of compounds, called "periodic compounds," identified by the selection rule $\bar{G} = \Sigma d_i e_i / \Sigma d_i$, where \bar{G} assumes the integral values 1, 2, 3, . . . corresponding to the periodic groups I, II, III, . . . , is discussed. The number of bonding electrons contributed by an atom of kind i is designated e_i , and d_i gives the number, per formula weight, of atoms of this kind. Both e_i and d_i assume integral values. Periodic compounds consist of symmetrical and unsymmetrical types. The recent synthesis of the unsymmetrical periodic compound B_2O , an isoelectronic analog of carbon, suggests that many more unsymmetrical types may be amenable to synthesis, particularly by high-pressure and high-temperature techniques.

The high-pressure, high-temperature synthesis of B_2O ,¹ an isoelectronic analog of carbon, has opened the door to the possible synthesis of a host of compounds that have not been considered before. Isoelectronic substances contain the same average number of valence electrons per atom. Thus, in the compound of composition B_2O there are two boron atoms with three valence electrons each and one oxygen atom with six valence electrons. This adds up to a total of 12 valence electrons for three atoms, which gives an average of four valence electrons per atom. Carbon, which is in the same row of the periodic table (principal quantum number $n = 2$) as boron and oxygen, has four valence electrons per atom. Consequently, B_2O is an isoelectronic analog of carbon, and such analogs display both similar and different properties.

Table 1. Isoelectronic analogs of carbon which utilize two kinds of atoms. The numbers in parentheses are the absolute values of the electronegativity difference of the combining atoms.

Symmetrical	Unsymmetrical	
BN (1.0)	BeN ₂ (1.5)	B ₂ O (1.5)
BeO (2.0)	LiN ₃ (2.0)	B ₃ F (2.0)
LiF (3.0)	Li ₂ O ₃ (2.5)	Be ₃ F ₂ (2.5)

The compound B_2O is an "unsymmetrical" analog of carbon and, as such, is the first representative of its kind. It is classed as unsymmetrical because boron and oxygen are

not symmetrically disposed with respect to the location of carbon in the periodic table. Boron has an atomic number, Z , of 5, whereas Z is 6 for carbon and 8 for oxygen. On the other hand, the compound BN with Z 's of 5 and 7 is symmetrical with respect to carbon. Symmetrical analogs of group IV elements in the periodic table are well known and have been much studied because of their importance as abrasives (low Z elements), semiconductors, photoconductors, and so forth. Examples of such compounds are BN, AlP, GaAs, InSb, ZnS, AgI, and CdTe. Apparently the unsymmetrical isoelectronic analogs have been completely overlooked; and I now report a way to identify and systematize them along with the symmetrical analogs.

All the possible (symmetrical and unsymmetrical) analogs of carbon which utilize two kinds of atoms are listed (Table 1) along with the difference in electronegativity Δx of the two kinds of combining atoms. The greater the electronegativity difference Δx , the less the compound is like carbon. Thus, BN simulates carbon most closely and is known in both a graphite and diamond-like form. High pressure and high temperature are required to transform "graphitic" BN to "diamond" BN²; this is also the case for transforming ordinary graphite to diamond.³ Beryllium oxide is known in a diamond-like form (hexagonal wurtzite structure) with tetrahedral bonding. The bonding in BeO, however, is probably more ionic than covalent. The compound LiF is known only in a rock-salt structure where ionic bonding prevails and resembles carbon the least. The new compound B_2O has hexagonal crystal symmetry related to graphite and may also exist in a diamond-like form (attempts to make the diamond form are encouraging but inconclusive). It should be possible to prepare the compound BeN₂ in a form as closely related to carbon as B_2O is. Next in line in similarity stand LiN₃, B₃F, and finally the pair Be₃F₂ and Li₂O₃ which should bear more resemblances to carbon than does LiF.

Tables similar to Table 1 could also be given which show the analogs of Si, Ge, Sn, and Pb. However, examples of "cross-compound" group IV analogs are given in Table 2 to illustrate another point. An average principal quantum number \bar{n} may be defined for cross-compounds as follows: $\bar{n} = \Sigma c_i n_i / \Sigma c_i$, where n_i is the

principal quantum number of an atom of kind i , and c_i is the number, per formula unit, of atoms of this kind.⁴ The average principal quantum number \bar{n} and the electronegativity difference Δx are very important factors in determining whether or not chemical bonding is directional or nondirectional in character. Mooser and Pearson⁴ have demonstrated this fact by preparing a graph (Fig. 1) in which the points Δx and \bar{n} are plotted for all AX-type compounds (such as NaCl, MgO, BN, and others) whose structures are known. Although Fig. 1 was prepared for symmetrical compounds, it should serve as a rough guide for predicting the type of bonding that might be possible in the unsymmetrical compounds such as are listed in Tables 1 and 2. Obviously, the compounds with the strongest tetrahedral bonds will be those with the lowest values of Δx as well as \bar{n} . Such compounds will probably require high pressure and temperature and possibly a catalyst for their synthesis. Strongly directed bonds are less mobile than other types. High temperatures are usually required to loosen them, catalysts are often needed to orient atoms for forming them, and high pressure is sometimes required for forcing them into place. Once in place, the activation energy for mobilizing these bonds is often so high that thermodynamically unstable compounds continue to exist "permanently" in spite of rather drastic conditions to which they might be subjected.

Table 2. Group IV, cross-compound analogs composed of elements with principal quantum number $n = 2$ and $n = 3$. The average principal quantum number \bar{n} of the compound is also listed along with the electronegativity difference Δx of the combining atoms. Compounds followed by asterisks are symmetrical.

Comp.	Δx	\bar{n}	Comp.	Δx	\bar{n}
LiCl*	2.0	2.5	NaF*	3.1	2.5
Li ₂ S ₃	1.5	2.6	Na ₂ O ₃	2.6	2.4
LiP ₃	1.1	2.8	NaN ₃	2.1	2.2
Be ₃ Cl ₂	1.5	2.4	Mg ₃ F ₂	2.8	2.6
BeS*	1.0	2.5	MgO*	2.3	2.5
BeP ₂	0.6	2.7	MgN ₂	1.8	2.3
B ₃ Cl	1.0	2.2	Al ₃ F	2.5	2.8
B ₂ S	0.5	2.3	Al ₂ O	2.0	2.7
BP*	0.1	2.5	AlN*	1.5	2.5
CSi*	0.7	2.5	SiC*	0.7	2.5

Table 3. Periodic compounds (binaries). Each numerical configuration represents a number of possible compounds: for example 2₃7₂ represents such compounds as Be₃F₂, Zn₃Cl₂, and Hg₃I₂, or any compound in which three atoms of one kind each contribute two electrons and two atoms of another kind each contribute seven electrons to chemical bonding. \bar{G} indicates the periodic group, II, III, VI . . ., being simulated. Absence of subscript indicates a subscript 1.

\bar{G}	Configurations
II	1 ₅ 7, 1 ₄ 6, 1 ₃ 5, 1 ₂ 4, 1 3
III	1 ₃ 6 ₂ , 1 ₂ 7, 1 4 ₂ , 1 5; 2 ₄ 7, 2 ₃ 6, 2 ₂ 5, 2 4
IV	1 ₂ 6 ₃ , 1 5 ₃ , 1 7; 2 ₃ 7 ₂ , 2 5 ₂ , 2 6; 3 ₃ 7, 3 ₂ 6, 3 5
V	1 6 ₄ , 1 7 ₂ ; 2 ₂ 7 ₃ , 2 6 ₃ ; 3 6 ₂ , 3 7; 4 ₂ 7, 4 6
VI	1 7 ₅ ; 2 7 ₄ ; 3 7 ₃ ; 4 7 ₂ ; 5 7

Table 4. Periodic compounds (ternaries). Nomenclature is the same as indicated in Table 3 with the addition at n , when it appears as a subscript, may assume any value.

\bar{G}	Configurations
II	1 ₉ 6 7, 1 ₈ 5 7, 1 ₇ 4 7, 1 ₇ 5 ₆ , 1 ₆ 3 7, 1 ₆ 4 6, 1 ₅ 2 _n 7, 1 ₅ 3 6, 1 ₅ 4 5, 1 ₄ 2 _n 6, 1 ₄ 3 5, 1 ₃ 2 _n 5, 1 ₃ 3 4, 1 ₂ 2 _n 4, 1 2 _n 3
III	1 ₅ 6 ₂ 7, 1 ₄ 5 6 ₂ , 1 ₃ 3 _n 6 ₂ , 1 ₃ 4 ₂ 7, 1 ₃ 5 7, 1 ₂ 3 _n 7, 1 ₂ 4 ₂ 5, 1 ₂ 4 6, 1 2 ₂ 5 ₂ , 1 2 ₂ 7, 1 2 4 ₃ , 1 2 6, 1 3 _n 4 ₂ , 1 3 _n 5; 2 ₇ 6 7, 2 ₆ 5 7, 2 ₅ 4 7, 2 ₅ 5 6, 2 ₄ 3 _n 7, 2 ₄ 4 6, 2 ₃ 3 _n 6, 2 ₃ 4 5, 2 ₂ 3 _n 5, 2 3 _n 4
IV	1 ₃ 5 6 ₄ , 1 ₃ 6 ₃ 7, 1 ₂ 2 6 ₄ , 1 ₂ 4 _n 6 ₃ , 1 ₂ 5 ₃ 7, 1 2 3 ₇ , 1 2 5 ₅ , 1 3 ₃ 7 ₂ , 1 3 5 ₄ , 1 3 6 ₂ , 1 4 _n 5 ₃ , 1 4 _n 7, 1 5 6; 2 ₄ 6 7 ₂ , 2 ₃ 4 _n 7 ₂ , 2 ₃ 5 ₄ 6, 2 ₂ 5 ₂ 6, 2 ₂ 5 7, 2 3 ₄ 6 ₃ , 2 3 ₂ 6 ₂ , 2 3 5 ₃ , 2 3 7, 2 4 _n 5 ₂ , 2 4 _n 6; 3 ₅ 6 7, 3 ₄ 5 7, 3 ₃ 4 _n 7, 3 ₃ 5 6, 3 ₂ 4 _n 6, 3 4 _n 5
V	1 2 ₂ 7 ₅ , 1 2 6 ₇ , 1 3 6 ₆ , 1 3 7 ₃ , 1 4 ₂ 7 ₃ , 1 4 6 ₅ , 1 5 _n 6 ₄ , 1 5 _n 7 ₂ , 1 6 ₂ 7; 2 ₂ 3 7 ₄ , 2 ₂ 5 _n 7 ₃ , 2 3 6 ₅ , 2 4 6 ₄ , 2 4 7 ₂ , 2 5 _n 6 ₃ , 2 6 7; 3 ₂ 6 ₂ 7, 3 4 ₂ 7 ₂ , 3 4 6 ₃ , 3 5 _n 6 ₂ , 3 5 _n 7; 4 ₃ 6 7, 4 ₂ 5 _n 7, 4 5 _n 6
VI	1 2 7 ₉ , 1 3 7 ₈ , 1 4 7 ₇ , 1 5 7 ₆ , 1 6 _n 7 ₅ ; 2 3 7 ₇ , 2 4 7 ₆ , 2 5 7 ₅ , 2 6 _n 7 ₄ ; 3 4 7 ₅ , 3 5 7 ₄ , 3 6 _n 7 ₃ ; 4 5 7 ₃ , 4 6 _n 7 ₂ ; 5 6 _n 7

Covalent bonds, particularly tetrahedral bonds, in addition to being characteristic of abrasive materials (in the low Z elements and compounds), are intimately connected with solid-state electronic properties. Consequently, all compounds falling below the line in the Mooser-Pearson chart are of interest from this standpoint.

The discussion above has been centered around compounds which simulate group IV elements. These compounds could be called

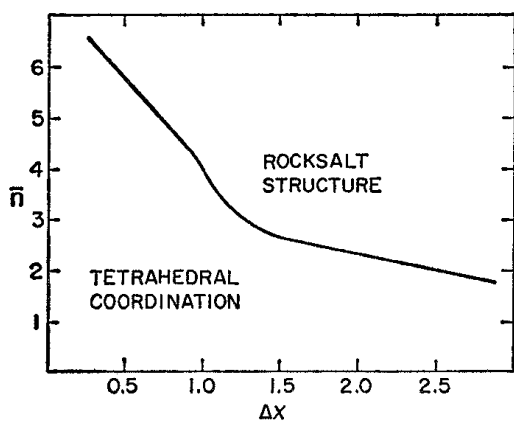


Fig. 1. Mooser-Pearson chart showing the line of demarcation between ionic and covalent bonding in AX type compounds. Electronegativity difference Δx for the elements A and X comprising the compound is plotted against the average principal quantum number \bar{n} of the compound.

group IV compounds. This concept can be extended to include compounds that simulate the properties of elements in other groups of the periodic table. For example, the compounds SiS and AlS₂ are analogs of phosphorus, and Si₂Br and GeO are cross-compounds akin to group V atoms. These four compounds could be classed as group V compounds. Similar compounds could be listed that would be classified as group II, III, and VI compounds. It is proposed that any compound that is isoelectronic with the elements of a periodic group be called a "periodic compound." The period compounds discussed so far have been made up from only two kinds of atoms. This is a needless restriction. Lists of periodic compounds containing three or more atoms can also be prepared.

From the above discussion, it now becomes possible to state the selection rule for finding periodic compounds. It is $\bar{G} = \sum d_i e_i / \sum d_i$, where \bar{G} assumes the integral values 1, 2, 3, . . . corresponding to the periodic groups I, II, III . . . , e_i is the number of bonding electrons contributed by an atom of kind i , and d_i is the number, per formula weight, of atoms of this kind. For this discussion, e_i and d_i assume only integral values. This rule, with the above-stated conditions, will include the elements and intragroup compounds such as SiC as period compounds.

Neglecting elements and intragroup compounds, a complete list of binary (two kinds of atoms) configurations that simulate group II

through group VI elements is given in Table 3. Each configuration represents a number of compounds. All the possible compounds are obtained from the table by permuting the elements with appropriate electron valence through the table. For example, the numerical configuration 1₂6₃ represents such compounds as Li₂O₃, K₂Te₃, and Cu₂S₃, or any compound in which two atoms of one kind each contribute one electron, and three atoms of another kind each contribute six electrons to bonding.

Table 4 presents the ternary configurations. Again the elements and intragroup compounds have been omitted.

Extensive lists of specific periodic compounds, together with \bar{n} and Δx values, compiled from Tables 3 and 4⁵ should be of value to any contemplating the synthesis of new solid-state materials, whether they be abrasives, thermoelectric substances, semiconductors, or photosensitive compounds. Research workers studying reactions at high pressure should find periodic compounds of interest for a number of reasons: (i) While most of the symmetrical periodic compounds are known, only a very few unsymmetrical compounds have come to light. Although the unsymmetrical far outnumber the symmetrical types, conventional synthesis procedures have apparently failed to disclose many of them. Therefore, it would seem worthwhile to utilize the newly available tool of combined high pressure and temperature in attempting the synthesis of these periodic compounds. (ii) Diamond and diamond-like BN and probably hexagonal B₂O are thermodynamically stable only at high pressure. Consequently, high pressure is required for their synthesis. Many of the proposed periodic compounds will also be stable only at high pressure, but, like diamond, may be retained in a metastable state by reducing the temperature required for synthesis to that of room temperature before the pressure required for synthesis is reduced to normal atmospheric pressure. (iii) Regardless of the necessity of using high pressure for thermodynamic reasons, it is sometimes needed for containing reactants which may be very volatile at the temperature required for synthesis. Present day high-pressure equipment is rapidly becoming a routine tool and can easily contain such substances as sulfur at 1800°C.

Only a small fraction of the total effort in research at high pressure is devoted to chemical synthesis, partly because there have been so few

guidelines to point the way to a useful goal. The synthesis of the periodic compounds, particularly of the unsymmetrical variety, should be a new test for the chemist's ingenuity.

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References and Notes

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⁶ Supported by NSF.

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