

set of any cycle in the preceding 100 years. If it is true that new-cycle activity as vigorous as that already shown by cycle 20 will continue to increase in spite of hemispheric asymmetries, then it is indeed probable that the minimum between cycles 19 and 20 has been passed.

The IQSY programs designed to study geophysical circumstances during 1964 and 1965 were undertaken in the hope of studying the earth-sun system under circumstances of solar quiet. The minimum of 1954, with its long intervals without spots or significant plages, was fresh in the memory of many of the planners. That 1964 failed to provide similarly long periods of solar quiet is all too apparent when summed values for area times intensity ($\Sigma \text{ area} \times \text{intensity}$) for the calcium plages for each day in 1954 are compared with similar data for 1964. However, in spite of the higher level of solar activity in 1964, there were many more days when geomagnetic indices were very low ($\Sigma K_p \leq 4$ and ≤ 9) in 1964 than in 1954 (see Fig. 7). This anomaly appears to be only part of the somewhat peculiar overall relationships that have existed during the last 32 years between geomagnetically quiet days and solar activity (see Fig. 8). Factors other than the phase and magnitude of the solar activity cycle appear to have influenced strongly the number of days per year on which the earth's magnetic field was without significant disturbance. If the geomagnetic indices K_p are truly homogeneous for the 32-year interval for which they are available, some explanation should be sought for the large numbers of geomagnetically quiet days in the period 1934–36 and the relatively small number of quiet days in 1954–55. Circumstances that favor extreme quiet in the earth's magnetic field may be almost as hard to recognize as those that lead to severe disturbance. These problems will be met, and perhaps answered, through the IQSY programs, already formulated, for the detailed study of chosen intervals of "quiet earth" and "quiet sun."

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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 table 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.

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 be-

cause 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" BN (2); 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 BeN_2 in a form as closely related to carbon as B_2O is. Next in line in similarity stand LiN_3 , B_3F , and finally the pair

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_2O (1.5)
BeO (2.0)	LiN_3 (2.0)	B_3F (2.0)
LiF (3.0)	Li_2O_3 (2.5)	Be_3F_2 (2.5)

Be₃F₂ and Li₂O₃ which should bear more resemblance 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

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 ₃ 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, 2₃7₃ represents such compounds as Be₃F₃, Zn₃Cl₃, and Hg₃I₃, 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 ₆ , 1 ₅ , 1 ₄ , 1 ₃
III	1 ₈ 6 ₂ , 1 ₇ , 1 ₄ , 1 ₅ ; 2 ₇ , 2 ₆ , 2 ₅ , 2 ₄
IV	1 ₂ 6 ₃ , 1 ₅ , 1 ₇ ; 2 ₃ 7 ₂ , 2 ₅ , 2 ₆ ; 3 ₇ , 3 ₆ , 3 ₅
V	1 ₆ , 1 ₇ ; 2 ₇ , 2 ₆ ; 3 ₆ , 3 ₇ ; 4 ₇ , 4 ₆
VI	1 ₇ , 2 ₇ ; 3 ₇ , 4 ₇ ; 5 ₇

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

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

another point. An average principal quantum number $\bar{n}$ may be defined for cross-compounds as follows: $\bar{n} = \sum c_i n_i / \sum c_i$, 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 Pearson (4) 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.

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 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

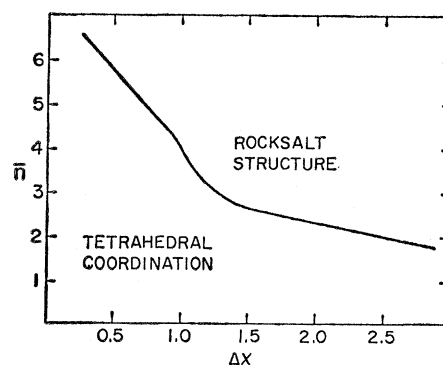


Fig. 1. Mooser-Pearson chart showing the line of demarcation between ionic and covalent bonding in AX type compounds. Electronegativity difference Δx for the elements A and X comprising the compound is plotted against the average principal quantum number $\bar{n}$ of the compound.

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 iso-electronic with the elements of a periodic group be called a "periodic compound." The periodic 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 periodic 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 4 (5) should be of value to anyone 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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Immunologic Tolerance in Thymectomized, Irradiated Rats Grafted with Thymus from Tolerant Donors

Abstract. *Lewis rats, thymectomized at 5 weeks of age and irradiated at 8 weeks, received grafts of adult thymus and marrow, one or both grafts being derived from donors tolerant to bovine γ -globulin. Challenge 3 or 6 weeks after grafting showed that delayed sensitization could not be induced in animals which received a tolerant thymus or tolerant thymus and marrow, though sensitization to a heterologous antigen (chicken ovalbumin) occurred normally. Arthus reactivity was regained slowly in animals receiving normal thymus and marrow and, to an equal extent, in those receiving grafts from tolerant donors.*

Specific acquired tolerance may be defined as the inability of an individual to respond immunologically to antigens with a particular constellation of determinant groups. It is induced by massive or repeated exposure to antigen in the perinatal period or in the adult rendered nonreactive temporarily by irradiation, treatment with alkylating agents, antimetabolites, or similar substances (1). It is also induced in the adult by administration of antigen in a form not readily phagocytized by cells of the reticuloendothelial system, for example, bovine γ -globulin (BGG) from which all aggregated material has been removed by ultracentrifugation (2), or by long-continued dosage of antigen (3). There is much evidence to suggest that this immunological nonreactivity is related to the persistence of antigen at an undetermined site and that phenomena designated by such terms as tolerance, paralysis, and unresponsiveness may be determined by the same underlying mechanism (1). Gowans has shown that tolerance, in two quite different immunologic systems (homograft immunity and antibody formation against sheep erythrocytes), is a property of the recirculating pool of small lymphocytes (4). It is not yet known whether this represents the presence of antigenic determinants within these cells at a sensitive site or the absence from the lymphocyte population of clones of cells reactive to the specific determinants. Nor is it clear whether the process that leads to tolerance, which must involve both lymphocytes and antigen, occurs in the peripheral lymphoid organs, in the circulation, or in

the source organs where lymphocytes are formed.

We have attempted to assess the role of two possible source organs, the bone marrow and the thymus (5, 6), in the development of tolerance by grafts of these organs from tolerant donors to thymectomized, irradiated recipients that were then challenged with specific antigen at varying intervals. Lewis rats (Microbiological Associates) are made tolerant to BGG by intraperitoneal doses of 20 mg at birth and 50 mg at 4 weeks. They fail to respond at 8 weeks to immunization with BGG, in that they do not develop skin reactivity of the Arthus type (presumably dependent on the presence of circulating antibody) or of the delayed type. In our experiment, normal rats were thymectomized at 5 weeks of age and re-

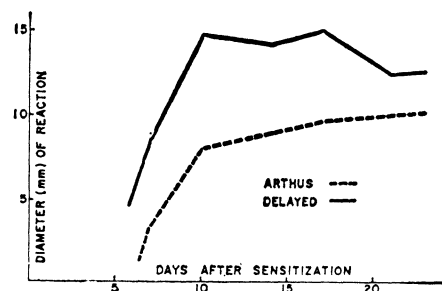


Fig. 1. Course of sensitization in group of six male Lewis rats sensitized by injection of 500 μ g of bovine γ -globulin (BGG) in adjuvant into one footpad and skin-tested with 30 μ g of BGG at 7, 10, 14, 17, 21, and 23 days. Average values for Arthus reactions (soft edematous lesions, maximal at 4 hours) and delayed reactions (indurated lesions, maximal at 24 hours) are plotted separately.