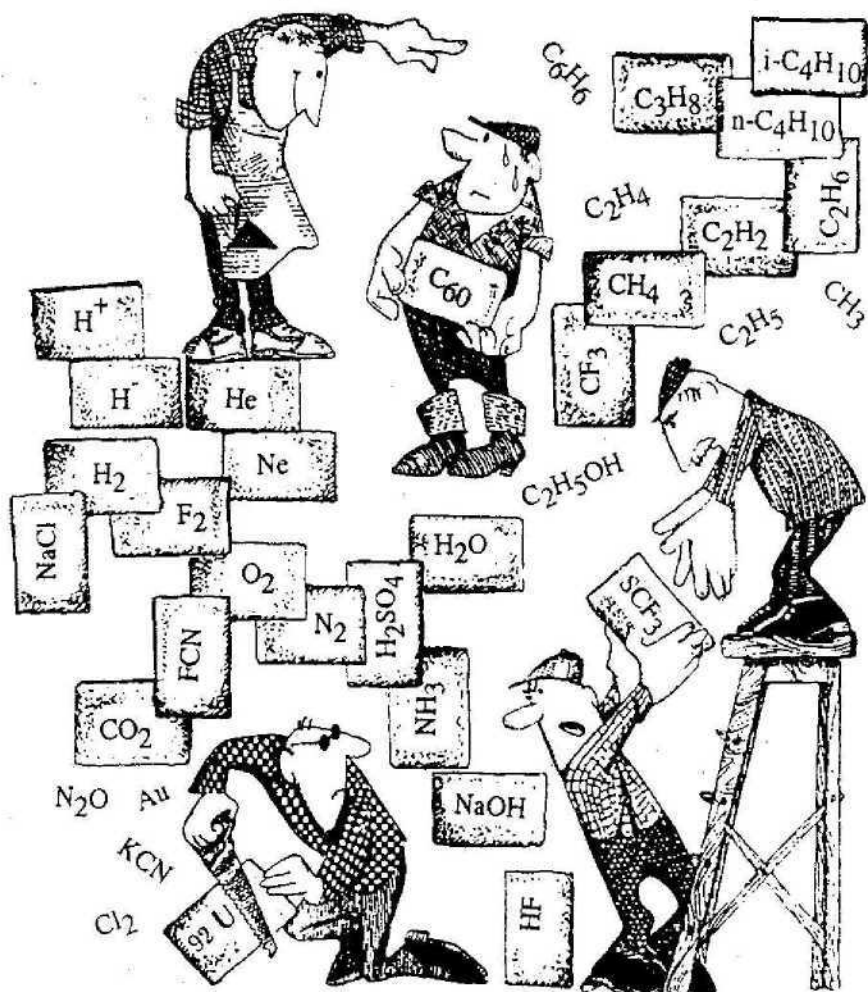


CHAPTER 3

The Concepts of Periodicity and Hyperperiodicity: from Atoms to Molecules

E.V. Babaev and R. Hefferlin



1. Origin of Periodicity

We meet with periodicity when something is repeated in time or in space. Periodic processes – like the rotations of planets, changes of seasons, high and low tides – are examples of global (all-pervading) periodicity in our solar system and in nature. Ancient astronomers and astrologers used some of these periodicities to regulate the activities of individuals and even of nations. Periodicity is an essential part of our life, as evidenced by the beating of our hearts and our eating, sleeping, and waking patterns. Geometrical or physical objects that are repeated in space (such as infinite mosaics or atoms in crystals) express other familiar examples of periodicity.

Because periodicity is such an important phenomenon, scientists have been interested in it for several centuries. Mathematicians describe periodicity in terms of periodic functions such as $F(X) = F(X + nT)$, where X is a time or space coordinate, $F(X)$ is a function describing something variable that repeats its value after every addition of the constant value T (the period) to the argument X , and n is an integer. The classical periodic functions $Y = \sin X$ and $Y = \cos X$ behave in this way, with clear alternations of maxima and minima. It is easy to imagine regular processes that are 'almost periodic' with a variable period T (for instance, if one eats or sleeps irregularly) or with changes in the amplitude of $F(X)$, as in the damped saw-tooth curves shown in Figure 1. In a case such as that in Figure 1, a strict mathematical

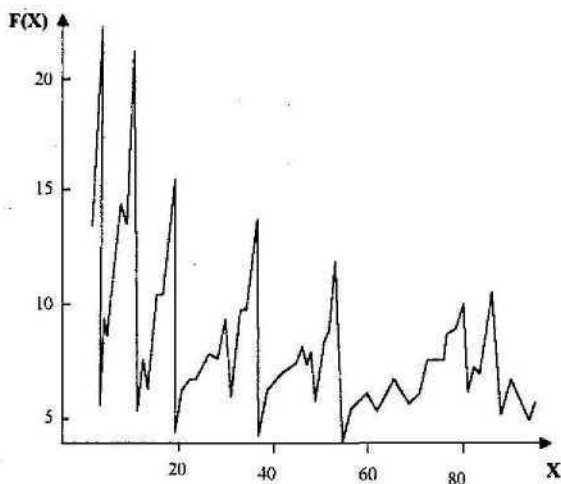


Figure 1 Example of an 'almost periodic' function (ionization potentials of atoms against their atomic numbers).

definition of the periodic function would be somewhat difficult. Nevertheless, it is only common sense that such a function can be treated as a periodic one. Such a qualitative, approximate understanding of periodicity and periodic functions has been widely adopted by the chemical community since the classical work at the end of the last century, leading up to the periodic table.

2. The Periodic Table

By the middle of the last century chemists generally understood that chemical elements can be grouped together in separate classes according to obvious similarities or dissimilarities in their properties. Thus, flammable alkali metals (that form stable cations) can be naturally separated from poisonous halogens (that prefer to form anions). It had also been demonstrated by Döbereiner that some elements may be grouped into triads so that the middle element's properties can be approximated as the average of the properties of its neighbors. Clarification of the concept of atomic weight by Cannizzaro in 1858 stimulated attempts to find a rational classification of the elements. In the 1850s-1890s several workers combined the principle of triads and chemical similarity, and used the atomic weights (really masses) of the elements to formulate the periodic law (see Table 1).

The idea of periodicity is expressed in Mendeleev's periodic chart, Figure 2. In this table the elements are arranged in rows (according to increasing atomic mass) and columns (according to chemically similar behavior) as in other early tables. However, only Mendeleev used this chart to predict previously unknown elements and to improve the known atomic masses of some elements (see Section 2.1). For simplicity, the elements of the table can be numbered in order of increasing atomic charge, though the physical meaning of such numbers was explained only a few decades later.

What sort of periodicity is expressed by this chart? Qualitatively speaking, the periodicity displayed here is simply the regular appearance of element-analogs with increasing atomic mass. Thus, the elements with numbers 3, 11, 19, 37, 55 are alkali metals, and those with numbers 9, 17, 35, 53 are halogens. It can be seen that the lengths of the rows (periods) in the periodic table are different and equal to 2, 8, 8, 18, 18, and 32. A mathematician would claim that there is no exact periodicity, since the period itself is not of constant value.¹¹ From the chemical viewpoint, however, it is a very important matter to place each element (especially each heavy element) such that its chemical nature resembles that of lighter elements. As a result, a lot of attempts have been undertaken by generations of chemists to express this non-exact periodicity in different graphic forms of the periodic table. Many examples have been collected in books,^{2,3,12,13} and we refer here only to few specially interesting cases (Figures 3a-c), such as the spiral, helical, and 'dumb-bell' forms.

2.1 Its Chemical Uses

The law of periodicity has stimulated better understanding of the interrelationships between elements, the design of new classes of compounds, and the search for and discovery of new elements. The topic has been extensively reviewed in many books,^{2-4,10-12,17-20} and according to a comprehensive review⁴ the total number of references related to chemical periodicity up to 1969 had reached 3000.

The heuristic role of the periodic table was recognized very clearly at the end of the last century. At that time it was proved that many macroscopic properties of elements (such as density, atomic volumes, and melting points) could be treated as periodic-like functions. Also, a method for the quantitative calculation of the

TABLE 1 Some Milestones in the Discovery of the Periodic Table

Contributor	Year	Contribution
Döbereiner	1829	Classification of elements into triads [1]
Kremers	1852	Development of rational classifications of elements and regularities in their atomic weights [2-4]
Gladston	1853	
Cooke	1854	
Lessen	1857	
Pettenkofer	1858	
Dumas	1858	
Strecker	1859	
Hinrichs	1867	
Odling	1857, 1864	Table of 43 elements arranged in 13 groups [5]
De Chancourtois	1862	Classification of elements (spiral around cylinder) with increase of their atomic weights [6]
Meyer	1864, 1871	Arranging of similar elements in groups, periodicity of atomic volumes [7]
Newlands	1865	Law of Octaves [8]
Mendeleev	1869, 1871	Periodic table; prediction of new elements and their properties; changes/improvements of known atomic weights [9,10]

Доклад ...
...
Менделѣевъ

The chart was written and autographed by Mendeleev

Handwritten notes and corrections:
 H=1 ?=2
 Be=9.4 Mg=24 Zn=65.2
 B=11 Al=27.4 ?=68
 C=12 Si=28 ?=70
 N=14 P=31 As=75
 O=16 S=32 Se=79.4
 F=19 Cl=35.5 Br=80
 Li=7 Na=23 K=39 Rb=85.4
 Ca=40 Sr=87.6
 ?=45 Ce=92
 ?Er=56 La=94
 ?Yl=80 Di=95
 ?In=75.6 Th=118?
 Ti=50 Zr=90 ?=150
 V=51 Nb=94 Ta=182
 Cr=52 Mo=96 W=186
 Mn=55 Rh=104.4 Pt=197.4
 Fe=56 Ru=104.4 Ir=198
 Ni=Co=59 Pt=106.6 Os=199
 Cu=63.4 Ag=108 Hg=200
 Cd=112
 U=116 Au=197.7
 Sn=118
 Sb=122 Bi=210.7
 Te=128?
 I=127
 Cs=133 Tl=204
 Ba=137 Pb=207
 ?=45 Ce=92
 ?Er=56 La=94
 ?Yl=80 Di=95
 ?In=75.6 Th=118?

ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ,
 ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ

The table presented to the Russian Chemical Society by Mendeleev

H=1	Be=9.4	Mg=24	Zn=65.2	Ti=50	Zr=90	?=150
B=11	Al=27.4	?=68	U=116	V=51	Nb=94	Ta=182
C=12	Si=28	?=70	Sn=118	Cr=52	Mo=96	W=186
N=14	P=31	As=75	Sb=122	Mn=55	Rh=104.4	Pt=197.4
O=16	S=32	Se=79.4	Te=128?	Fe=56	Ru=104.4	Ir=198
F=19	Cl=35.5	Br=80	I=127	Ni=Co=59	Pt=106.6	Os=199
Li=7	Na=23	K=39	Rb=85.4	Cu=63.4	Ag=108	Hg=200
		Ca=40	Sr=87.6	Cd=112		
		?=45	Ce=92			
		?Er=56	La=94			
		?Yl=80	Di=95			
		?In=75.6	Th=118?			

One century later, 1969:
 A one rouble coin with Mendeleev



Modern form of the periodic table

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103															
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu			
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr			

Figure 2 The Periodic Table of the elements.

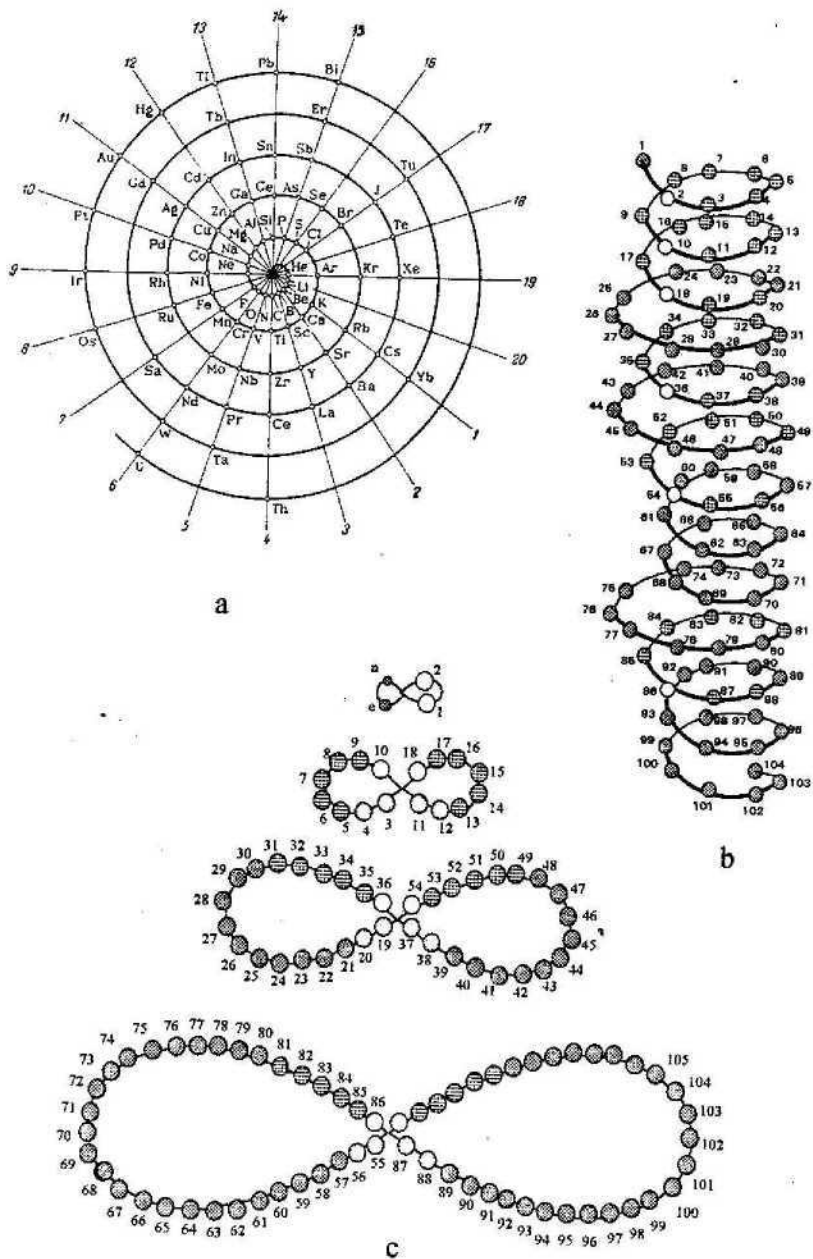


Figure 3 Examples of different non-traditional forms of the periodic chart for the elements: (a) the spiral form due to Baumgauer,¹⁴ (b) the helical form due to Bilecki,¹⁵ and (c) the 'dumb-bell' form due to Basset.¹⁶ (Adapted from ref. 13.)

macroscopic properties of new (or even unknown!) elements was developed (Table 2). This method (most consistently and successfully used by Mendeleev) included comparison of the properties of all the neighbors of a given element in the periodic table. An element is surrounded by a maximum of eight neighbors; it thus belongs to four triads (horizontal, vertical and two diagonal triads). An analysis of the trends in properties in each triad provides a way to estimate any unknown property. This methodology, equally applicable to elements and their compounds, opened up the possibility of estimating desired properties with high accuracy (see Table 2). However, this general method of comparative calculation of elemental properties is rather rarely used in practice. Instead, nowadays, chemists use the Periodic Law (and the periodic chart) to analyze qualitative (but not quantitative) trends in different properties of the elements. This opportunity to see general chemical trends directly from the periodic chart is of great importance in modern chemical education. Indeed, it is easy to distinguish (say) metals from non-metals at first glance in the 'school' periodic chart, by locating them respectively at the lower left and upper right corners of the table.

2.2 Its Physical Explanation

The modern interpretation of the periodic table appeared after the development of the physical model of the atom as a positively charged nucleus surrounded by negatively charged electrons. Atoms of different elements differ by the charge (number of protons) in their nuclei. This hypothesis, which was proved experimentally,³⁰ explained the element numbers in the periodic table as a set of natural physical invariants for atoms.

Moreover, an explanation has been given for the irregular lengths of the rows in the periodic table as well as for the origin of groups with chemically similar elements. The electrons of every atom can be subdivided into shells, and each shell can hold a different number of electrons. The shells are concentric about the nucleus. Atoms with a fixed number of electrons in the inner shells correspond to a row of elements in the periodic table, while atoms with a constant number of electrons in the outer shell correspond to a group of elements. The electrons in the outer shell are usually called valence electrons, since they are responsible for chemical bonding and their number is connected with the chemical valency of the atom. Thus, the periodic system is constructed (and can be explained) on the basis of the isoelectronic principle: atoms are arranged as isovalent families (vertical groups) and 'iso-inner-electronic' families (horizontal rows). The different numbers of electrons that can be held by the inner shells reflect the different lengths of the periods observed in the periodic table.

It is significant that not only the macroscopic properties of elements, but also many of the microscopic properties of atoms, demonstrate pronounced periodicity. Examples of such properties include the atomic radius and volume, ionization potential, electron affinity, electronegativity, and some optical and magnetic properties.^{2,4,17-20} The function in Figure 1 is actually the first ionization energy of atoms plotted against their atomic number.

TABLE 2 Use of the Periodic Table for Prediction of Elements and Their Properties in the Nineteenth Century

Element ^{a)}	Prediction of element/property ^{b)} principal researcher, date	Experimental discovery contributor, date
Ga	Eka-Aluminium (Ea) M=68, d=5.9, low m.p. Mendeleev, 1869-71 ^{9,10}	Gallium M=69.72, d=5.904, m.p.=30 Lecoq de Boisbandran, 1875-76 ²¹
Sc	Eka-Boron (Eb) M=44, d (Eb ₂ O ₃)=3.5 Mendeleev, 1869-71 ^{9,10}	Scandium M=45.1, d (Sc ₂ O ₃)=3.864 Nilson, 1879-80 ²²
Ge	Eka-Silicium (Es), M=72, d=5.5 d (EsO ₂)=4.7; b.p.(EsCl ₄)=90 Mendeleev, 1869-71 ^{9,10}	Germanium, M=72.5 d=5.35 d (GeO ₂)=4.703; b.p.(GeCl ₄)=86 Winkler, 1886 ²³
Ne Kr, Xe	New gaseous element, M=20 Elements analogous to He and Ar Ramsay, 1895-97 ²⁴	Neon, M=19.96 Krypton, Xenon Ramsay, Travers, 1897-98 ²⁵
Be	Decrease of atomic weight (1.5 times) Mendeleev, 1869 ^{9,10} , Brauner, 1878 ²⁶	Nilson, Petersen, 1884 ²⁷
In	Increase of atomic weight (1.5 times) Mendeleev, 1869-70 ^{9,10} , Meyer, 1870 ⁷	Bunzen, Mendeleev, 1871 ²⁸
Ce, Y, Er	Increase of atomic weights (1.5 times)	Brauner, 1881; Cleve, 1875;
U, Th	Increase of atomic weights (2 times) Mendeleev, 1869-71 ^{9,10}	Roscoe, 1874; Rammelsberg, 1872 ²⁹

^{a)}Actually predicted by use of the periodic table and discovered later. ^{b)}M - atomic weight; d - density (g/cm³); m.p./b.p. melting/boiling point (°C); changes of atomic weights from those accepted in 1869.

3. Periodic Systems in Other Sciences

The beauty of the periodic system of the elements exerted a strong influence on other sciences. Indeed, there are a lot of objects that can be generally considered as 'elements'. One can consider ions, atomic nuclei (isotopes of elements), elementary particles and quarks as examples of such objects in physics. In addition, in many descriptive disciplines (mineralogy, organic chemistry, botany, zoology) there are enormous numbers of closely related objects that require natural classifications. In many cases scientists have developed classifications – with the periodic table in mind as the standard of excellence. Some attempts have been made to generalize the meaning of the terms 'natural' and 'periodic' systems in order to develop a general methodology of classification in science and to consider the system of chemical elements as an important special case.

3.1 Some Known Criteria for Natural Systems

An early attempt to give general criteria for natural systems was made by the entomologist and philosopher Lyubischev. It was his dream (first conceived in the 1920s and later developed in the 1970s) to construct a periodic system of living organisms.³¹ Although he did not achieve his general goal, Lyubischev formulated many stimulating ideas about natural systems; his papers on general taxonomy and classification,³² as well as his philosophical works, pointed out their true value.³³ According to one of his definitions, 'a system should be considered as natural if the position of an element in it reflects the maximum number of elemental properties.' In spite of some vagueness in this definition, it opens up the possibility of developing new systems and improving existing ones. It is easy to see that the periodic table is an excellent example of the validity of this general principle; other examples are also discussed below.

Another important criterion for natural systems was developed in the 1970s by Urmantsev, another Russian biologist. He discussed some original parallels between isomerism in chemistry and in biology (e.g. the structural peculiarities of non-identical leaves on the same tree or of petals in the flowers in his rather intriguing 'periodic system of flowers').³⁴ Urmantsev seems to be the first to have considered the special case of 'systems of objects of a given genus', and he tried to formulate some of their general properties.^{34,35} One important principle is that any element of such a system should possess the property of polymorphism. (Originally, the phenomenon of polymorphism was observed in mineralogy; there, it is the property of a mineral compound to exist in more than one crystalline form, for example, octahedral and cubic.)

Considered globally, this principle of polymorphism reflects the idea that any kind of element (that is claimed to be a simple one) may be complex; indeed any 'simple element' may actually consist of simpler parts. A triad of concepts – the nature, number, and interrelations of these smaller parts – should be taken into account, otherwise the polymorphism will appear as an inexplicable property. In the simplest case polymorphism may be caused by different geometrical interrelation of elemental parts. Urmantsev illustrated this principle in his table of flowers, where the

number of petals is fixed, but the petals can be arranged in a geometrically different manner.³⁴ Chemical isomerism^{36,37} is a good example of such global polymorphism; the term 'isomerism' (in a broader sense) has also been accepted in biology³⁸ and nuclear physics.³⁹ An example of polymorphism for the elements in the periodic table is the well-known phenomenon of allotropy⁴⁰ (e.g. the existence of the element carbon as diamond or graphite). Yet again, isotopes, ions, and excited states of atoms also illustrate the possibilities of different polymorphism types for elements.

3.2 Criteria for Periodic Systems

Dias has attempted to formulate general criteria and properties for a periodic table set.⁴¹ In attempting to classify polycyclic benzenoids and their analogs (see Section 4.1.1), Dias came up with a periodic system of aromatic hydrocarbons. Making parallels between his tables and the periodic chart, Dias proposed the following criteria for a periodic table set:

1. It is a partially ordered set (i.e. it obeys reflexivity, antisymmetry, transitivity);
2. It is two-dimensional and of infinite extent; and
3. It complies with the triad principle (any central element has a metric property that is the arithmetic mean of two oppositely adjacent elements).

Also among the properties of a periodic table set mentioned by Dias are (i) hierarchical ordering, (ii) periodicity of at least one invariant, (iii) edge effects (i.e. elements on at least one two-dimensional edge have values for various properties which are more extreme than those for elements chosen at random), and (iv) the greatest difference is frequently to be found in the properties of the smallest element.

3.3 Periodic Systems of Subatomic Objects

Elementary particles. High-energy physics has resulted in the discovery of a great number of 'elementary' particles. There are three leptons, each with its antiparticle; each of these six objects has its own neutrino. Then there are mesons, which were originally defined as having masses between that of the electron and the proton but now defined on the basis of their having integer spin. These mesons come in groups of one, or two, or three with almost the same mass value. As groups having larger and larger masses are studied, some of them appear to be very similar to less massive groups; these particles are excited forms of the least massive particles. Thus, there are hundreds of mesons but only a few are in their ground state. Exactly the same situation pertains to baryons, which are particles with masses equal to (or greater than) that of the proton and with half-integer spin. Some of their groups even have four particles. Two important invariants – the average charge and the isotopic spin – can be used^{42,43} to arrange multiplets of elementary particles in periodic tables. In Figure 4, such a grouping (which pertains to the SU(3) version of the standard model of fundamental particle physics) is shown for some mesons (Figure 4, left) and

baryons (Figure 4, right) in their ground states. The periodicity here is that such diagrams are repeated at higher masses for excited particles. In theoretical physics such diagrams can be constructed from first principles, namely by a combination of analogous diagrams for quarks, which are sub-elementary particles.

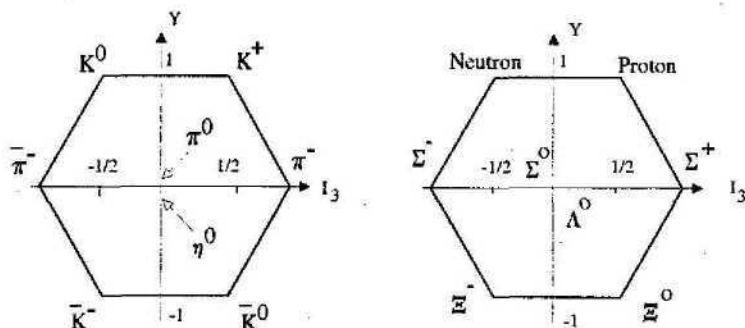


Figure 4 Left: The $J^P = 0^-$ multiplet of mesons. Right: The $J^P = 1/2^+$ multiplet of baryons. I_3 is the isotopic spin and Y is the hypercharge; both of these quantities are related to the charges of particles and of groups of particles. The Greek letters π , η , Σ , Λ , and Ξ refer to various elementary particles aside from the neutron and proton. The signs indicate whether the particles have positive, neutral, or negative charge with magnitudes equal to that of the electron; a bar over the particle symbol indicates that it is an antiparticle. (Taken with permission and adapted from ref. 43.)

Isotopes. The classification of isotopes is another well-developed field.^{11,12,44,45} The number of known isotopes is over 1700 and exceeds the number of known atoms by a large factor. It was mentioned early on that the stability of isotopes is connected with 'magic numbers' of nucleons: protons, neutrons, and sometimes their sum. In this sense, there is a parallelism between stable nucleonic configurations (the isotopes with the magic numbers 2, 8, 20, 50 etc.) and atoms with closed shells (magic numbers 2, 10, 18 etc., for atoms of the noble gases). The periodic system of isotopes can be expressed in several alternative ways, as in Figure 5. One such table proposed in the 1960s by Selinov⁴⁵ and designed as a seven-colored wall-chart is shown in Figure 6. The bold zig-zag line on this table that connects black squares (stable isotopes) reflects the idea of periodicity.

Ions. One intriguing problem that arises from the periodic table of atoms is the possibility of constructing periodic systems of ions.⁴⁶ An atom can be completely or partially ionized to a cation by removing electrons, or transformed into an anion by the addition of new electrons. In Figure 7 the energy required for a few consecutive ionizations of atoms is plotted against the atomic number. One can see that the curves are periodic, and hence it is possible to construct periodic tables for mono-, di- and multi-charged cations. If we look at the dispositions of the maxima and minima of the curves and compare them with those for atoms, it becomes evident that the magic numbers of electrons for ions are the same as for neutral atoms. Therefore, the

	2	8	14	20	28	50	82	126, N					
Nr													
1	I	II	Ca	III	Sr	IV	Ba	V	Ra				
2		I	Ca	II	Zr	III	Nd	IV	Po				
3	I	II, III	Ca	IV	Ge	V	Sn	VI	W				
4		I	Ar	II	Sr	III	Ce	IV	Pb				
5	I	O	II	Si	III	Fe	IV	Sr	V	Sn	VI	Ba	
6		I	Si	II	Ni	III	Sr	IV	Sn	V	Ce	VI	Pb
	2	8	14	20	28	50	82	Z					

Figure 5 Possible periodic tables of the isotopes; vertical lines separate the periods in the Valley of Stability. (N – number of nucleons, Z – number of protons).

number of electrons (but not the charge on the nucleus) is responsible for the periodicity of ions.

4. Molecular Periodicity

Progress in periodic classifications of objects smaller than atoms leads to the fascinating question: is it possible to apply the idea of periodicity to molecules? Can we construct, analogously to the chart for atoms, a periodic chart for molecules – organic, inorganic, and organometallic molecules? Can we imagine a *natural* system where the role of an ‘element’ can be played by a molecule, so that the position of an object in such a system reflects the data for a maximum number of the molecular properties?

Such ideas have been around for a very long time and are related to the general problem of classification of chemical compounds; they have in fact stirred the thoughts of many scientists since the middle of the last century. The French chemist Gerhardt in the 1840s proposed playing a game of chemical ‘patience’ with cards that would place homological and heterological series of molecules in a natural arrangement.⁴⁷ He then added smaller and smaller pieces of paper (isological series) on every card of his patience game to classify compounds in formal three-dimensional space. The Russian chemist Butlerov was seriously interested in Gerhardt’s idea, but failed to integrate isomers into such a three-dimensional system, and so finally criticized and rejected it.⁴⁸

Many contributors to the Periodic Law (in particular, Dumas, Pettenkofer, and Newlands)⁴⁹ have described parallels between triads of the elements and members of homological series of hydrocarbons differing by a CH_2 -group (see also Section 4.1.1). In 1862, Newlands presented two of many tables exhibiting the composition and mutual relations of organic substances and serving as ‘a map of organic chemistry’ (see^{49c}). The tables show, along vertical, horizontal, and upper-left/lower-right and upper-right/lower-left diagonals, bodies differing by H_2 , O and CO_2 (among others) or bodies in which one such symbol is replaced by another. Later,

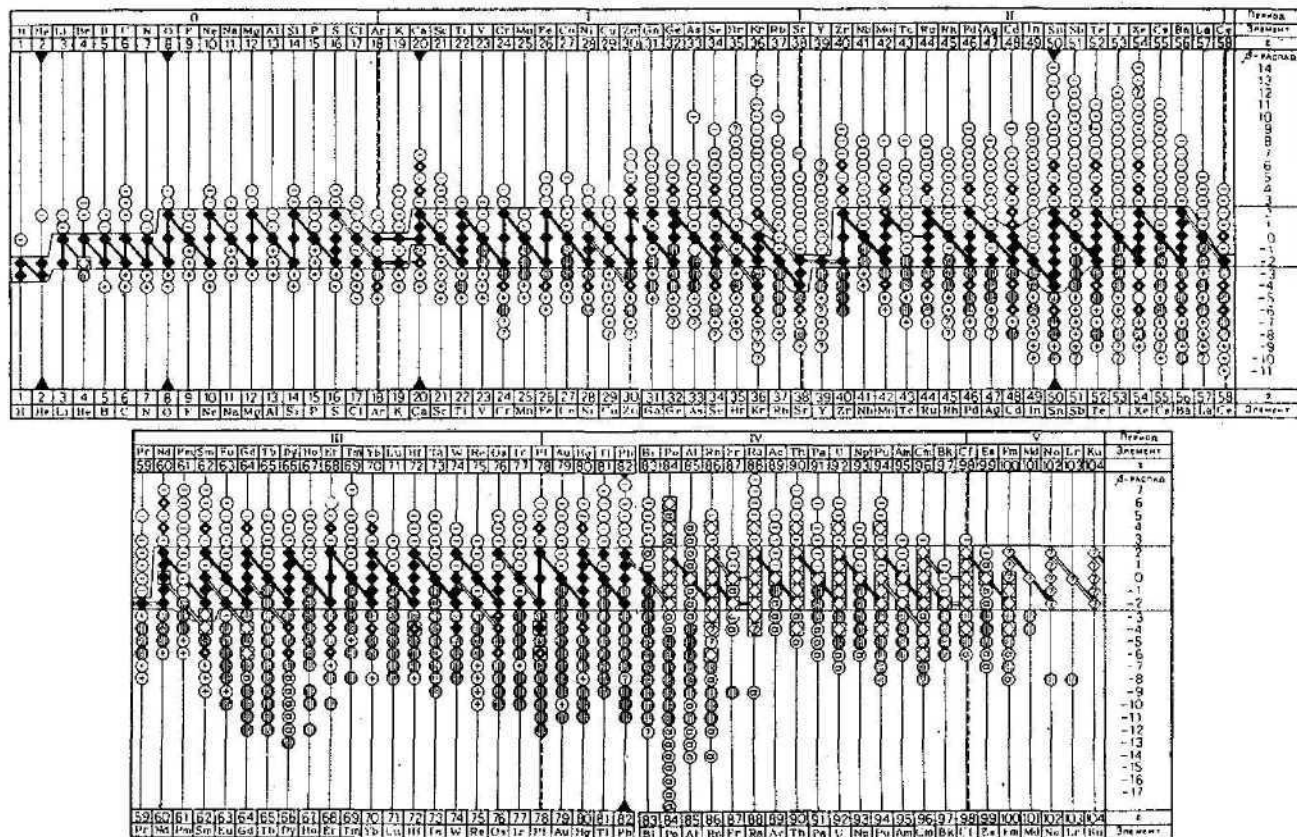


Figure 6 The periodic table of isotopes (the wall-chart of I. Selinov). The running axis (1 to 104) indicates the element. The perpendicular axis indicates the excess of neutrons over protons. The black triangles indicate the magic numbers of protons.

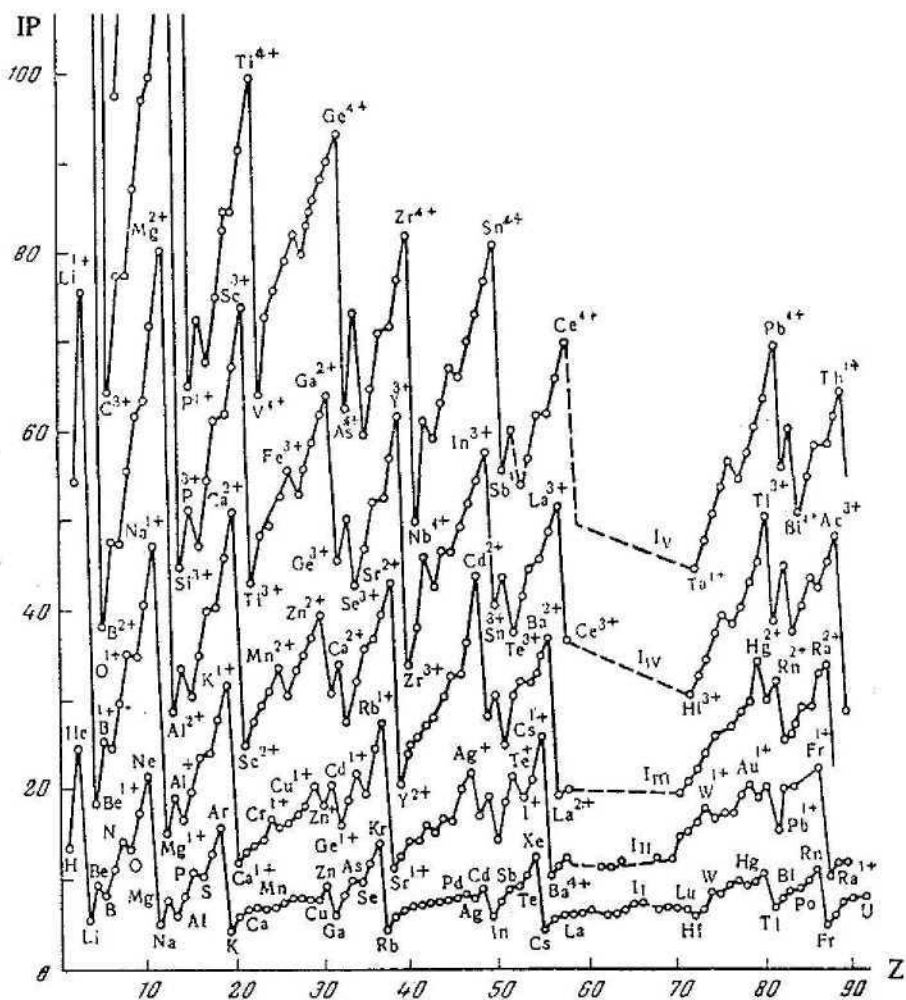


Figure 7 Successive ionization potentials of atoms plotted against atomic numbers can be used to construct a period table of ions.

Pelopidas mentioned parallelism between series of organic radicals with decreasing degree of saturation and elements in rows (see ref. 49d). Thus, the saturated methylammonium radical CH_3NH_3 is analogous to an alkali metal, while the unsaturated radical CN behaves similarly to a halogen.

After the discovery of the Periodic Law, many attempts – some intuitive and others based on a solid mathematical and physical background – have been made to study the problem of molecular periodicity. The present chapter sets itself the goal of reviewing the general methodology, the history, and recent progress in this interesting field. Early results on this topic can be found in the authors'

publications^{43,50-52} and in the monograph of Gorsky.⁵³

4.1 How to Talk about Molecular Periodicity

Let us first distinguish the *local* and the *global* approaches to molecular periodicity. The local approach seeks to classify a separate (finite or infinite) subset of molecules; the global approach seeks to classify all sets of possible molecules. The local models of molecular classification are more widespread, are characterized by a great diversity of viewpoints, and in some cases their authors refer to such models as 'periodic tables'. Let us consider a few impressive examples of such local tables from organic chemistry and from inorganic chemistry.

4.1.1 Local Models: Examples of Diversity

Periodic table of hydrocarbons. As we mentioned above, a lot of parallels between the elements and hydrocarbons were discussed in nineteenth century.⁴⁹ One elegant attempt to express this analogy in graphical form was made by the Russian Morozov.⁵⁴ In his table of hydrocarbon radicals (Figure 8) the homological hydrocarbons are arranged in columns in the same way as are similar elements in the periodic chart. Moreover, he drew many curious analogies between the organic radicals and corresponding elements (parallelisms in atomic and molecular mass, maximal valency, and acidic and basic properties of corresponding hydroxides). It is less known that in the first version of his table (distributed in 1885)⁵⁵ Morozov predicted the existence of a whole column of 'nonvalent' elements (appearing as analogs of the paraffins), calculated their atomic weights (namely, 4, 20, 36, and 82) and proposed their arrangement in the periodic table (see also ref. 10c, p. 135, and ref. 12, p. 51). Although the idea was criticized and rejected by contemporaries, nevertheless, a decade later,^{24,25} these elements were found: the noble gases! It is interesting that Morozov wrote his giant book in the Schlisselburg Fortress during his 25 years of incarceration for his pamphlets against the Russian Czar's family.^{55a} The book with the table, therefore, finally appeared in 1907 (long after the discovery of the noble gases); when Mendeleev read it, he was so impressed with its content that he immediately had Morozov appointed to a full professorship: the silver lining in the cloud of his imprisonment!

Another model called the 'Natural System of Hydrocarbon Compounds' was proposed in 1922 by Decker.⁵⁶ The system was simply a two-dimensional plane with the numbers of the carbon and hydrogen atoms on the axes. Such oversimplified classification, however, has appeared useful in comparisons of known types of organic homology (vinylogy, phenylogy, benzannelation etc.) and the design of novel types of homological series.

Periodic table of functional groups (paraelements). In the 1980s Haas, in trying to explain the halogen-like properties of the pseudohalogen groups (e.g. CF_3 , SCF_3 , CN , NCO , N_3) proposed⁵⁷ the so-called 'element displacement principle'. In his model, certain radicals with element-like behavior (the paraelements) can be designed by the formal addition of x ligands (atoms or other paraelements) to prototype p-elements with a corresponding shift of x places to the right within the

Два периодических системы.

I — Система нормальных алифатических углеводородов в их первичной метамерии (ключ системы водород — H₁).

II — Система современных минеральных элементов — «археогелидов» (ключ системы гелий).

H ₁								He								
2								4								
			C	CH	CH ₂	CH ₃	CH ₄	Li	Be	B	C	N	O	F	Ne	
			12	13	14	15	16	3+1	3+1	10+1	12	14	16	18+1	20	
			C ₂	C ₂ H	C ₂ H ₂	C ₂ H ₃	C ₂ H ₄	Na	Mg	Al	Si	P	S	Cl	Ar	
			24	25	26	27	28	29	30	22+1	24	26+1	28	30+1	32	36+4
CH	CH ₂	CH ₃	C ₂ H ₄	C ₂ H ₅	C ₂ H ₆	C ₂ H ₇	C ₂ H ₈	K	Ca	Sc	Ti	V	Cr	Mn	Fe	
37	38	39	40	41	42	43	44	38+1	40	44	48	50+1	52	55-56	58-59	
CH ₃	C ₂ H ₄	C ₂ H ₅	C ₂ H ₆	C ₂ H ₇	C ₂ H ₈	C ₂ H ₉	C ₂ H ₁₀	Cu ²⁺	Zn	Ga	Ge	As	Se	Br	Kr	
51	52	53	54	55	56	57	58	62+1	64	70	72	74+1	78+1	80	82?	
C ₂ H ₅	C ₂ H ₆	C ₂ H ₇	C ₂ H ₈	C ₂ H ₉	C ₂ H ₁₀	C ₂ H ₁₁	C ₂ H ₁₂	Rb	Sr	Yt	Zr	Nb	Mo	Rh	Pd	
65	66	67	68	69	70	71	72	84+1	86+1	88+1	90	92+1	96	102+1	102-107	
C ₂ H ₇	C ₂ H ₈	C ₂ H ₉	C ₂ H ₁₀	C ₂ H ₁₁	C ₂ H ₁₂	C ₂ H ₁₃	C ₂ H ₁₄	Rg	Cd	In	Sn	Sb	Te	I	Xe	
79	80	81	82	83	84	85	86	108	112	114	118+1	120	126+1	128+1	128+1	
C ₂ H ₉	C ₂ H ₁₀	C ₂ H ₁₁	C ₂ H ₁₂	C ₂ H ₁₃	C ₂ H ₁₄	C ₂ H ₁₅	C ₂ H ₁₆	Cs	Ba	La	Ce	Pr	Nd	Pm	Sa	
89	94	95	96	97	98	99	100	132+1	136+1	138	138+1	140-144	146	148	150	
C ₂ H ₁₁	C ₂ H ₁₂	C ₂ H ₁₃	C ₂ H ₁₄	C ₂ H ₁₅	C ₂ H ₁₆	C ₂ H ₁₇	C ₂ H ₁₈									
107	108	109	110	111	112	113	114	152	156	158	160-162	162	170	172	172?	
C ₂ H ₁₃	C ₂ H ₁₄	C ₂ H ₁₅	C ₂ H ₁₆	C ₂ H ₁₇	C ₂ H ₁₈	C ₂ H ₁₉	C ₂ H ₂₀	Er	Cs	Zr	Ta	W	Re	Os	Pt	
121	122	123	124	125	126	127	128	172?	174?	178?	180	182+1	184	192+1	194-196	
C ₂ H ₁₅	C ₂ H ₁₆	C ₂ H ₁₇	C ₂ H ₁₈	C ₂ H ₁₉	C ₂ H ₂₀	C ₂ H ₂₁	C ₂ H ₂₂	Au	Hg	Sr	Pb	Bi	Po	At	Fr	
135	136	137	138	139	140	141	142	196+1	200	204	206+1	208	210?	214?	216?	
C ₂ H ₁₇	C ₂ H ₁₈	C ₂ H ₁₉	C ₂ H ₂₀	C ₂ H ₂₁	C ₂ H ₂₂	C ₂ H ₂₃	C ₂ H ₂₄									
149	150	151	152	153	154	155	156	222?	226?	228?	230?	232?	234?	236?	238?	
(1?) C ₂ H ₂₅	(3?) C ₂ H ₂₆	(4?) C ₂ H ₂₇	(5?) C ₂ H ₂₈	(6?) C ₂ H ₂₉	(7?) C ₂ H ₃₀	(8?) C ₂ H ₃₁	(9?) C ₂ H ₃₂	1	2	3	4	5	6	7	8	
173	174	175	176	177	178	179	180	173?	176?	178?	180	182+1	184	192+1	194-196	
(1?) C ₂ H ₃₃	(2?) C ₂ H ₃₄	(3?) C ₂ H ₃₅	(4?) C ₂ H ₃₆	(5?) C ₂ H ₃₇	(6?) C ₂ H ₃₈	(7?) C ₂ H ₃₉	(8?) C ₂ H ₄₀	7	6	5	4	3	2	1	0	
191	192	193	194	195	196	197	198	196+1	200	204	206+1	208	210?	214?	216?	
(1?) C ₂ H ₄₁	(2?) C ₂ H ₄₂	(3?) C ₂ H ₄₃	(4?) C ₂ H ₄₄	(5?) C ₂ H ₄₅	(6?) C ₂ H ₄₆	(7?) C ₂ H ₄₇	(8?) C ₂ H ₄₈	7	6	5	4	3	2	1	0	
217	218	219	220	221	222	223	224	222?	226?	228?	230?	232?	234?	236?	238?	
(1?) C ₂ H ₄₉	(2?) C ₂ H ₅₀	(3?) C ₂ H ₅₁	(4?) C ₂ H ₅₂	(5?) C ₂ H ₅₃	(6?) C ₂ H ₅₄	(7?) C ₂ H ₅₅	(8?) C ₂ H ₅₆	7	6	5	4	3	2	1	0	
235	236	237	238	239	240	241	242	222?	226?	228?	230?	232?	234?	236?	238?	
(1?) C ₂ H ₅₇	(2?) C ₂ H ₅₈	(3?) C ₂ H ₅₉	(4?) C ₂ H ₆₀	(5?) C ₂ H ₆₁	(6?) C ₂ H ₆₂	(7?) C ₂ H ₆₃	(8?) C ₂ H ₆₄	7	6	5	4	3	2	1	0	
253	254	255	256	257	258	259	260	222?	226?	228?	230?	232?	234?	236?	238?	

Figure 8 Formal analogy between the periodic tables of elements and hydrocarbon radicals due to Morozov.⁵⁴ The title: 'Two periodic systems'; subtitles: I — The system of normal aliphatic hydrocarbons (key to the system — hydrogen); II — The system of modern mineral elements 'archeogelids' (key to the system — helium). Bottom numbers: valency in respect of halogens and metals.

period of the periodic system. The paraelements, therefore, can be arranged into a set of periodic tables (Figure 9). Haas proved analogies between the elements and paraelements by means of extensive physical data (NMR shifts, dissociation enthalpies, electronegativities), structural features (interchangeability in known structures) and examples of chemical similarity. He is also currently applying this concept in the practical design of novel inorganic molecules and functional groups.

Periodic table of polycyclic hydrocarbons. Benzenoid hydrocarbons form an interesting series of molecules with delocalized bonds; it is easy to imagine such structures if one looks at a honeycomb with some cells full of honey. Dias has recently discussed⁴¹ many regularities within this class in terms of their periodic table (see Section 3.2). The parameters used to construct such a table are the internal structural features of fused polygons (Figure 10), and such parameters turn out to reflect many aspects of similarity among polyaromatic hydrocarbons.

4.1.2 Early Attempts of Global Classification

The periodic tables just described are elegant examples of local periodic tables. We now discuss the equally interesting approaches to a global periodic system of molecules. Two names should be mentioned in relation to the history of global molecular classifications. The first is the Russian Shemyakin who published in the 1930s a series of papers⁵⁸ under the title *Natural Classification of Chemical Compounds*. The other is the Pole Gorsky who developed in the 1970s the 'morphological' classification of compounds.^{53,59}

Shemyakin proposed the 'molecular number' – that is, the sum of the atomic numbers of all the atoms in a molecule (actually the total number of electrons) – as the basis of his classification. Evidently, such an approach immediately runs up against polymorphism: there is vast growth in the number of isoelectronic molecules with increase of molecular number. As a result, Shemyakin had to introduce additional parameters (such as the number of hydrogen atoms and the 'characteristic structural number' for isomers), and he used them to draw three-dimensional structure-property correlation charts for both organic and inorganic molecules (as in Figure 11a). Unfortunately, such charts include many senseless combinations of atoms and, therefore, it is somewhat difficult to use them in practice. Nevertheless, Shemyakin discussed at least nine classes of table (isostructural and isoelectronic, isoelectronic but not isostructural, etc.) that he declared to be the projections of a unique table of all molecules. (An example of a building block of such a table is presented on Figure 11b.) One result of his classification was his formulas to calculate boiling points of alkanes from the boiling points of the noble gases.

In the approach of Gorsky, inorganic molecules are classified by two parameters, e_v and e_z , that reflect changes of molecules in redox and acid-base reactions, respectively. The first number is the so-called 'normalized' oxidation number of the central atom (or of a few atoms), and the second number is the total charge of the ligands around the central core(s). Having used these parameters as the coordinates, Gorsky constructed many classification tables for different inorganic molecules (e.g. for oxy-acids of phosphorus and sulfur), drawing either concrete

C	N ≡CF	O =NF =CF ₂	F -OF -NF ₂ -CF₃	Ne F ₂ OF ₂ NF ₃ CF ₄	Na - - - (NF ₄)
Si	P ≡SF	S =PF =SF ₂	Cl -SF PF ₂ -SIF ₂	Ar ClF SF ₂ PF ₃ SIF ₄	K - (ClF ₂) (SF ₃) (PF ₄)
C	N ≡CCF ₂	O =NCF ₂ =C(CF ₃) ₂	F -OCF ₂ -N(CF ₃) ₂ -C(CF ₃) ₃	Ne CF ₃ -F (CF ₃) ₂ O (CF ₃) ₃ N (CF ₃) ₄ C	
Si	P ≡SiCF ₃	S =PCF ₂ =Si(CF ₃) ₂	Cl -SCF₃ -P(CF ₃) ₂ -Si(CF ₃) ₃	Ar CF ₃ -Cl (CF ₃) ₂ S (CF ₃) ₃ P (CF ₃) ₄ Si	
C	N ≡CSCF ₃	O =NSCF ₂ =C(SCF ₃) ₂	F -OSCF ₂ -N(SCF ₃) ₂ -C(SCF ₃) ₃	Ne CF ₃ SF (CF ₃ Si) ₂ O (CF ₃ Si) ₃ N (CF ₃ Si) ₄ C	
Si	P ≡SiSCF ₃	S =PSCF ₂ =Si(SCF ₃) ₂	Cl -SSCF ₃ -P(SCF ₃) ₂ -Si(SCF ₃) ₃	Ar CF ₃ SiCl (CF ₃ Si) ₂ S (CF ₃ Si) ₃ P (CF ₃ Si) ₄ Si	
C	N	O =CO =CS	F -NO -CN -NS	Ne O=O N=N O=S	
C	N CCN	O C=CO NCN C-CS	F NCO OCN NCS	Ne OCO FCN OCS	

Figure 9 Haas' periodic system of functional groups. The first and second diagrams show how Haas generalized Grimm's hydrogen displacement principle by the substitution of fluorine for hydrogen; he names these species 'paraelements'. The third and fourth diagrams show how an entry in the first diagram, CF₃, can be substituted for the fluorine in the first two diagrams. Haas designates the resulting species 'first-order derivative paraelements'. The fifth and sixth diagrams show how an entry in the fourth diagram, CF₃S, can be substituted for the CF₃ in the third and fourth diagrams. Haas designates the resulting species 'second-order derivative paraelements'. The seventh diagram shows what happens if ligands like oxygen, sulfur, or nitrogen are used; displacements of two or three groups must take place. The last diagram shows what happens if various of the paraelements of the seventh diagram are substituted with the appropriate displacements. The diagrams are from ref. 57; used with permission.

$(N_C = 3N_H - 14 - 2d_s)$																	
$N_C = 3N_H + 4$	$N_C = 3N_H + 2$	$N_C = 3N_H$	$N_C = 3N_H - 2$	$N_C = 3N_H - 4$	$N_C = 3N_H - 6$	$N_C = 3N_H - 8$	$N_C = 3N_H - 10$	$N_C = 3N_H - 12$	$N_C = 3N_H - 14$	$N_C = 3N_H - 16$	$N_C = 3N_H - 18$	$N_C = 3N_H - 20$	$(N_C = 2N_H - 6 + N_{IC})$				
Forbidden region							$N_C/N_H < 2$										
							C_6H_6	$C_{10}H_6$	$C_{14}H_6$	$C_{18}H_6$	$C_{22}H_6$	$C_{26}H_6$	$C_{30}H_6$	$C_{34}H_6$	$C_{38}H_6$	$C_{42}H_6$	$C_{46}H_6$
$N_C/N_H > 3$		$2 < N_C/N_H < 3$											$C_{22}H_{14}$	$N_C = 2N_H - 4$			
													$C_{24}H_{14}$	$N_C = 2N_H - 2$			
													$C_{26}H_{14}$	$N_C = 2N_H$			
													$C_{28}H_{14}$	$N_C = 2N_H + 2$			
$C_{30}H_{16}$ $C_{30}H_{12}$													$C_{30}H_{16}$	$N_C = 2N_H + 4$			
													$C_{32}H_{16}$	$N_C = 2N_H + 6$			
													$C_{34}H_{16}$	$N_C = 2N_H + 8$			
													$C_{36}H_{16}$	$N_C = 2N_H + 10$			
													$C_{38}H_{16}$	$N_C = 2N_H + 12$			
													$C_{40}H_{16}$	$N_C = 2N_H + 14$			
$C_{42}H_{18}$ $C_{42}H_{12}$													$C_{42}H_{18}$	$N_C = 2N_H + 16$			
													$C_{44}H_{18}$	$N_C = 2N_H + 18$			
													$C_{46}H_{18}$	$N_C = 2N_H + 20$			
													$C_{48}H_{18}$	$N_C = 2N_H + 22$			
													$C_{50}H_{18}$	$N_C = 2N_H + 24$			
													$C_{52}H_{18}$	$N_C = 2N_H + 26$			
$C_{54}H_{20}$ $C_{54}H_{12}$													$C_{54}H_{20}$	$N_C = 2N_H + 8$			
													$C_{56}H_{20}$	$N_C = 2N_H + 10$			
													$C_{60}H_{20}$	$N_C = 2N_H + 14$			
													$C_{62}H_{20}$	$N_C = 2N_H + 16$			
													$C_{66}H_{20}$	$N_C = 2N_H + 20$			
													$C_{68}H_{20}$	$N_C = 2N_H + 22$			
													$C_{70}H_{20}$	$N_C = 2N_H + 24$			
													$C_{72}H_{20}$	$N_C = 2N_H + 26$			
$C_{74}H_{22}$ $C_{74}H_{12}$													$C_{74}H_{22}$	$N_C = 2N_H + 10$			
													$C_{76}H_{22}$	$N_C = 2N_H + 12$			
													$C_{80}H_{22}$	$N_C = 2N_H + 18$			
													$C_{82}H_{22}$	$N_C = 2N_H + 20$			
													$C_{86}H_{22}$	$N_C = 2N_H + 26$			
													$C_{88}H_{22}$	$N_C = 2N_H + 28$			
$C_{90}H_{24}$ $C_{90}H_{12}$													$C_{90}H_{24}$	$N_C = 2N_H + 14$			
													$C_{92}H_{24}$	$N_C = 2N_H + 16$			
													$C_{96}H_{24}$	$N_C = 2N_H + 22$			
													$C_{98}H_{24}$	$N_C = 2N_H + 24$			
													$C_{102}H_{24}$	$N_C = 2N_H + 30$			
													$C_{104}H_{24}$	$N_C = 2N_H + 32$			
$C_{106}H_{26}$ $C_{106}H_{12}$													$C_{106}H_{26}$	$N_C = 2N_H + 16$			
													$C_{108}H_{26}$	$N_C = 2N_H + 18$			
													$C_{112}H_{26}$	$N_C = 2N_H + 26$			
													$C_{114}H_{26}$	$N_C = 2N_H + 28$			
													$C_{118}H_{26}$	$N_C = 2N_H + 34$			
													$C_{120}H_{26}$	$N_C = 2N_H + 36$			
$C_{122}H_{28}$ $C_{122}H_{12}$													$C_{122}H_{28}$	$N_C = 2N_H + 18$			
													$C_{124}H_{28}$	$N_C = 2N_H + 20$			
													$C_{128}H_{28}$	$N_C = 2N_H + 30$			
													$C_{130}H_{28}$	$N_C = 2N_H + 32$			
													$C_{134}H_{28}$	$N_C = 2N_H + 38$			
													$C_{136}H_{28}$	$N_C = 2N_H + 40$			
$C_{138}H_{30}$ $C_{138}H_{12}$													$C_{138}H_{30}$	$N_C = 2N_H + 18$			
													$C_{140}H_{30}$	$N_C = 2N_H + 20$			
													$C_{144}H_{30}$	$N_C = 2N_H + 30$			
													$C_{146}H_{30}$	$N_C = 2N_H + 32$			
													$C_{150}H_{30}$	$N_C = 2N_H + 40$			
													$C_{152}H_{30}$	$N_C = 2N_H + 42$			
$C_{154}H_{32}$ $C_{154}H_{12}$													$C_{154}H_{32}$	$N_C = 2N_H + 20$			
													$C_{156}H_{32}$	$N_C = 2N_H + 22$			
													$C_{160}H_{32}$	$N_C = 2N_H + 32$			
													$C_{162}H_{32}$	$N_C = 2N_H + 34$			
													$C_{166}H_{32}$	$N_C = 2N_H + 42$			
													$C_{168}H_{32}$	$N_C = 2N_H + 44$			
$C_{170}H_{34}$ $C_{170}H_{12}$													$C_{170}H_{34}$	$N_C = 2N_H + 20$			
													$C_{172}H_{34}$	$N_C = 2N_H + 22$			
													$C_{176}H_{34}$	$N_C = 2N_H + 32$			
													$C_{178}H_{34}$	$N_C = 2N_H + 34$			
													$C_{182}H_{34}$	$N_C = 2N_H + 44$			
													$C_{184}H_{34}$	$N_C = 2N_H + 46$			
$C_{186}H_{36}$ $C_{186}H_{12}$													$C_{186}H_{36}$	$N_C = 2N_H + 22$			
													$C_{188}H_{36}$	$N_C = 2N_H + 24$			
													$C_{192}H_{36}$	$N_C = 2N_H + 34$			
													$C_{194}H_{36}$	$N_C = 2N_H + 36$			
													$C_{198}H_{36}$	$N_C = 2N_H + 46$			
													$C_{200}H_{36}$	$N_C = 2N_H + 48$			
$C_{202}H_{38}$ $C_{202}H_{12}$													$C_{202}H_{38}$	$N_C = 2N_H + 24$			
													$C_{204}H_{38}$	$N_C = 2N_H + 26$			
													$C_{208}H_{38}$	$N_C = 2N_H + 36$			
													$C_{210}H_{38}$	$N_C = 2N_H + 38$			
													$C_{214}H_{38}$	$N_C = 2N_H + 50$			
													$C_{216}H_{38}$	$N_C = 2N_H + 52$			
$C_{218}H_{40}$ $C_{218}H_{12}$													$C_{218}H_{40}$	$N_C = 2N_H + 26$			
													$C_{220}H_{40}$	$N_C = 2N_H + 28$			
													$C_{224}H_{40}$	$N_C = 2N_H + 40$			
													$C_{226}H_{40}$	$N_C = 2N_H + 42$			
													$C_{230}H_{40}$	$N_C = 2N_H + 54$			
													$C_{232}H_{40}$	$N_C = 2N_H + 56$			
$C_{234}H_{42}$ $C_{234}H_{12}$													$C_{234}H_{42}$	$N_C = 2N_H + 28$			
													$C_{236}H_{42}$	$N_C = 2N_H + 30$			
													$C_{240}H_{42}$	$N_C = 2N_H + 42$			
													$C_{242}H_{42}$	$N_C = 2N_H + 44$			
													$C_{246}H_{42}$	$N_C = 2N_H + 56$			
													$C_{248}H_{42}$	$N_C = 2N_H + 58$			
$C_{250}H_{44}$ $C_{250}H_{12}$													$C_{250}H_{44}$	$N_C = 2N_H + 30$			
													$C_{252}H_{44}$	$N_C = 2N_H + 32$			
													$C_{256}H_{44}$	$N_C = 2N_H + 44$			
													$C_{258}H_{44}$	$N_C = 2N_H + 46$			
													$C_{262}H_{44}$	$N_C = 2N_H + 58$			
													$C_{264}H_{44}$	$N_C = 2N_H + 60$			
$C_{266}H_{46}$ $C_{266}H_{12}$													$C_{266}H_{46}$	$N_C = 2N_H + 32$			
													$C_{268}H_{46}$	$N_C = 2N_H + 34$			
													$C_{272}H_{46}$	$N_C = 2N_H + 46$			
													$C_{274}H_{46}$	$N_C = 2N_H + 48$			
													$C_{278}H_{46}$	$N_C = 2N_H + 60$			
													$C_{280}H_{46}$	$N_C = 2N_H + 62$			
$C_{282}H_{48}$ $C_{282}H_{12}$													$C_{282}H_{48}$	$N_C = 2N_H + 34$			
													$C_{284}H_{48}$	$N_C = 2N_H + 36$			
													$C_{288}H_{48}$	$N_C = 2N_H + 50$			
													$C_{290}H_{48}$	$N_C = 2N_H + 52$			
													$C_{294}H_{48}$	$N_C = 2N_H + 64$			
													$C_{296}H_{48}$	$N_C = 2N_H + 66$			
$C_{298}H_{50}$ $C_{298}H_{12}$													$C_{298}H_{50}$	$N_C = 2N_H + 36$			
													$C_{300}H_{50}$	$N_C = 2N_H + 38$			
													$C_{304}H_{50}$	$N_C = 2N_H + 52$			
													$C_{306}H_{50}$	$N_C = 2N_H + 54$			
													$C_{310}H_{50}$	$N_C = 2N_H + 66$			
													$C_{312}H_{50}$	$N_C = 2N_H + 68$			
$C_{314}H_{52}$ $C_{314}H_{12}$													$C_{314}H_{52}$	$N_C = 2N_H + 38$			
													$C_{316}H_{52}$	$N_C = 2N_H + 40$			
													$C_{320}H_{52}$	$N_C = 2N_H + 54$			
													$C_{322}H_{52}$	$N_C = 2N_H + 56$			
													$C_{326}H_{52}$	$N_C = 2N_H + 70$			
													$C_{328}H_{52}$	$N_C = 2N_H + 72$			
$C_{330}H_{54}$ $C_{330}H_{12}$													$C_{330}H_{54}$	$N_C = 2N_H + 40$			
													$C_{332}H_{54}$	$N_C = 2N_H + 42$			
													$C_{336}H_{54}$	$N_C = 2N_H + 56$			
													$C_{338}H_{54}$	$N_C = 2N_H + 58$			
													$C_{342}H_{54}$	$N_C = 2N_H + 72$			
													$C_{344}H_{54}$	$N_C = 2N_H + 74$			
$C_{346}H_{56}$ $C_{346}H_{12}$													$C_{346}H_{56}$	$N_C = 2N_H + 42$			
													$C_{348}H_{56}$	$N_C = 2N_H + 44$			
													$C_{352}H_{56}$	$N_C = 2N_H + 60$			
													$C_{354}H_{56}$	$N_C = 2N_H + 62$			
													$C_{358}H_{56}$	$N_C = 2N_H + 76$			
													$C_{360}H_{56}$	$N_C = 2N_H + 78$			
$C_{362}H_{58}$ $C_{362}H_{12}$													$C_{362}H_{58}$	$N_C = 2N_H + 44$			
													$C_{364}H_{58}$	$N_C = 2N_H + 46$			
													$C_{368}H_{58}$	$N_C = 2N_H + 62$			
													$C_{370}H_{58}$	$N_C = 2N_H + 64$			
													$C_{374}H_{58}$	$N_C = 2N_H + 80$			
													$C_{376}H_{58}$	$N_C = 2N_H + 82$			
$C_{378}H_{60}$ $C_{378}H_{12}$													$C_{378}H_{60}$	$N_C = 2N_H + 46$			
													$C_{380}H_{60}$	$N_C = 2N_H + 48$			
													$C_{384}H_{60}$	$N_C = 2N_H + 64$			
													$C_{386}H_{60}$	$N_C = 2N_H + 66$			
													$C_{390}H_{60}$	$N_C = 2N_H + 82$			
													$C_{392}H_{60}$	$N_C = 2N_H + 84$			
$C_{394}H_{62}$ $C_{394}H_{12}$													$C_{394}H_{62}$	$N_C = 2N_H + 48$			
													$C_{396}H_{62}$	$N_C = 2N_H + 50$			
													$C_{400}H_{62}$	$N_C = 2N_H + 66$			
													$C_{402}H_{62}$	$N_C = 2N_H + 68$			
													$C_{406}H_{62}$	$N_C = 2N_H + 84$			
													$C_{408}H_{62}$	$N_C = 2N_H + 86$			
$C_{410}H_{64}$ $C_{410}H_{12}$													$C_{410}H_{64}$	$N_C = 2N_H + 50$			
													$C_{412}H_{64}$	$N_C = 2N_H + 52$			
													$C_{416}H_{64}$	$N_C = 2N_H + 70$			
													$C_{418}H_{64}$	$N_C = 2N_H + 72$			
													$C_{422}H_{64}$	$N_C = 2N_H + 88$			
													$C_{424}H_{64}$	$N_C = 2N_H + 90$			
$C_{426}H_{66}$ $C_{426}H_{12}$													$C_{426}H_{66}$	$N_C = 2N_H + 52$			
													$C_{428}H_{66}$	$N_C = 2N_H + 54$			
													$C_{432}H_{66}$	$N_C = 2N_H + 72$			
													$C_{434}H_{66}$	$N_C = 2N_H + 74$			
													$C_{438}H_{66}$	$N_C = 2N_H + 90$			
													$C_{440}H_{66}$	$N_C = 2N_H + 92$			
$C_{442}H_{68}$ $C_{442}H_{12}$													$C_{442}H_{68}$	$N_C = 2N_H + 54$			
													$C_{444}H_{68}$	$N_C = 2N_H + 56$			
													$C_{448}H_{68}$	$N_C = 2N_H + 74$			
													$C_{450}H_{68}$	$N_C = 2N_H + 76$			
													$C_{454}H_{68}$	$N_C = 2N_H + 94$			
													$C_{456}H_{68}$	$N_C = 2N_H + 96$			
$C_{458}H_{70}$ $C_{458}H_{12}$													$C_{458}H_{70}$	$N_C = 2N_H + 56$			
													$C_{460}H_{70}$	$N_C = 2N_H + 58$			
													$C_{464}H_{70}$	$N_C = 2N_H + 76$			
													$C_{466}H_{70}$	$N_C = 2N_H + 78$			
													$C_{470}H_{70}$	$N_C = 2N_H + 96$			
													$C_{472}H_{70}$	$N_C = 2N_H + 98$			
$C_{474}H_{72}$ $C_{474}H_{12}$													$C_{474}H_{72}$	$N_C = 2N_H + 58$			
													$C_{476}H_{72}$	$N_C = 2N_H + 60$			
													$C_{480}H_{72}$	$N_C = 2N_H + 78$			
													$C_{482}H_{72}$	$N_C = 2N_H + 80$			
													$C_{486}H_{72}$	$N_C = 2N_H + 98$			
													$C_{488}H_{72}$	$N_C = 2N_H + 100$			
$C_{490}H_{74}$ $C_{490}H_{12}$													$C_{490}H_{74}$	$N_C = 2N_H + 60$			
													$C_{492}H_{74}$	$N_C = 2N_H + 62$			
													$C_{496}H_{74}$	$N_C = 2N_H + 80$			
													$C_{498}H_{74}$	$N_C = 2N_H + 82$			
													$C_{502}H_{74}$ </				

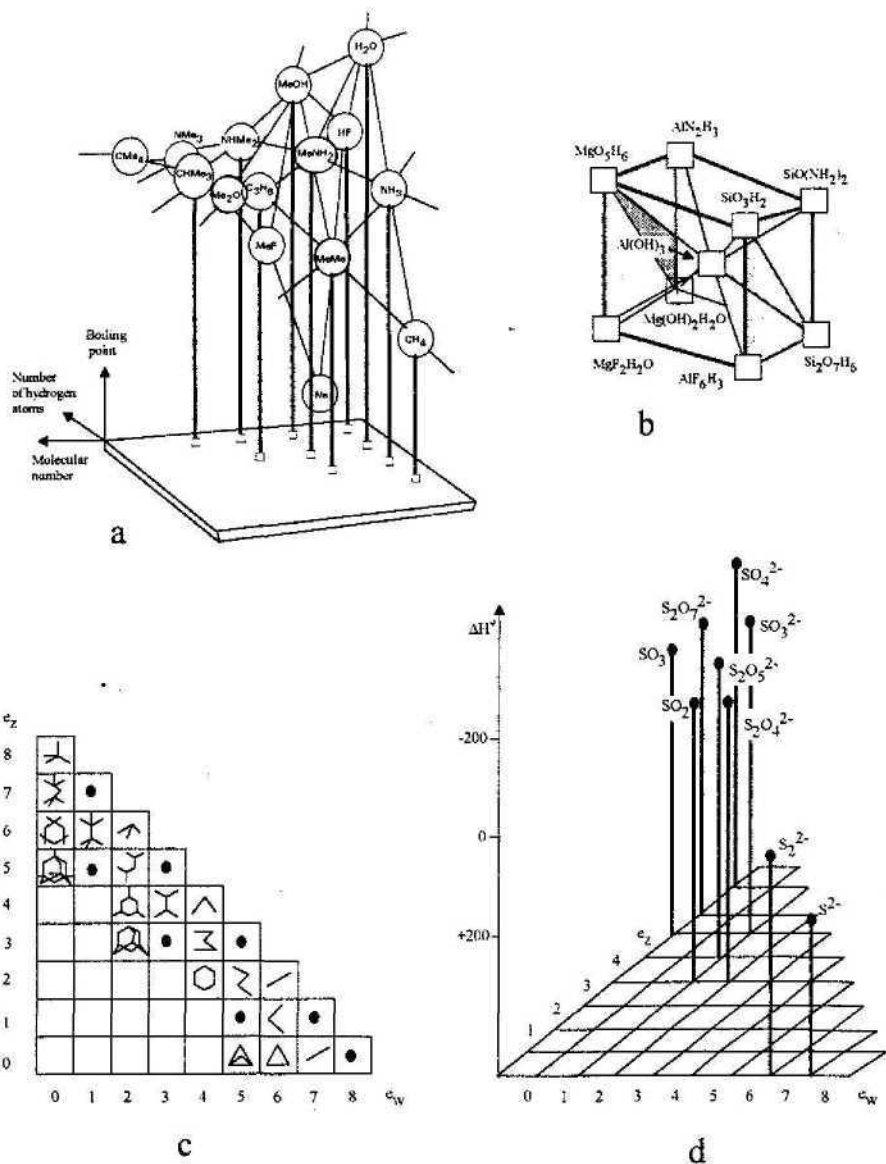


Figure 11 Early attempts at global classification by Shemyakin, (a) and (b),⁵⁸ and Gorsky, (c) and (d).⁵⁹ (a) three-dimensional graph with the number of hydrogen atoms and molecular number on the horizontal axes and boiling point on the vertical axis, (b) and (c) examples of building blocks for more complete classifications, (d) three-dimensional graph with parameters e_v and e_z (see text) on the horizontal axes and enthalpy on the vertical axis.

formulas or general structures, as in Figure 11c. He also illustrated the usefulness of such tables by constructing three-dimensional charts capable of predicting the thermodynamic properties of molecules, as shown in Figure 11d.

The above-mentioned global classifications have been neither adopted nor used by the general chemical community. Let us now try to analyze the underlying problem here.

4.1.3 Global Models: What to Classify and Why?

In order to clarify the problem of global molecular periodicity, we first attempt to answer some simpler questions: what are the objects and the goals of such a classification? In other words: what should we classify and why?

What to classify? In the case of elements we have *objects* (atoms or their condensed phases) and measurable *data* (microscopic and macroscopic properties) that form the basis for their periodic classification. In the case of molecules – if we consider them as the ‘elements’ of an alternative classification – problems may appear both in relation to the objects themselves (the existence and stability of an isolated molecule), their relation to the condensed phase, and even the possibility of measuring molecular properties.

Suppose we decide to compare only isolated molecules. In such a case we would still need to define clearly the meaning of the term ‘molecule’ in relation to the condensed phases. We usually define a molecule as an aggregate of chemically connected atoms (with given atomic numbers), that can be separated as an entity from surrounding media because of a greater stability – greater internal (intramolecular) forces than external (intermolecular) ones. Of course, the difference between such intra- and intermolecular forces depends on the nature of the atoms. On the other hand, in many cases this difference may not be large (say, for ionic crystals, alloys, or atomic lattices such as diamond), and it is somewhat difficult to identify a ‘molecule’ in the condensed phase.

The problem can be illustrated by use of the well-known⁶⁰ ‘Grimm Tetrahedron’ (Figure 12). This diagram symbolically uses the four vertices of a tetrahedron to represent the four main types of bonding in solid chemical compounds – i.e. metallic, ionic, atomic, and van der Waals. The six edges between these vertices correspond to the intermediate types of bonding. It is clear that the idea of isolated molecules can be most naturally applied only to one vertex of this diagram (the central one in Figure 12, where the intermolecular interactions are the weak van der Waals forces). Such compounds correspond to typical organic and (simple) inorganic molecules with covalent bonds. For the remaining types of bonding, the corresponding ‘molecules’ (formula units) may be unstable to the processes of self-association, and so lose their identities in the condensed phase under usual conditions. In such cases, special efforts must be made to vaporize the compound and investigate the structure and properties of its isolated molecules.

Among the set of theoretically possible molecules, those with covalent bonds predominate over those with the other three types of bond under typical ‘wet chemistry’ conditions. This suggests that (i) a global molecular classification should

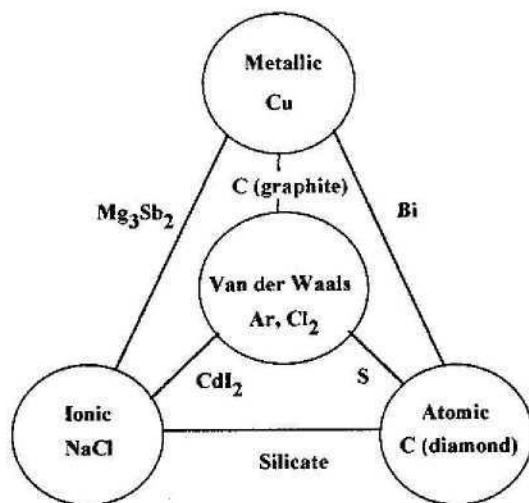


Figure 12 Different types of intermolecular bonding represented by chemical compounds on the vertices and edges of the 'Grimm tetrahedron' (see text).

be first addressed to covalently-bonded molecules, and that (ii) the problem of 'empty places' may turn out to be unavoidable for a global system until more representative data can be collected. This pronounced asymmetry between the ideal objects of classification and real molecules hindered for many years significant development of the entire area of molecular periodicity. Fortunately, in the past few decades, short-lived species and especially clusters have become more available for experimentalists. Major progress in spectroscopy and mass spectrometry, and the use of lasers and the matrix isolation technique, open up the possibility of studying their properties systematically. The development of quantum-chemical calculations provides an alternative route to the estimation of the properties of unstable molecules and clusters of almost any imaginable combination of atoms.

Why classify? There are several reasons. (i) A pragmatic aim: to arrange molecules in naturally related series in order to calculate any desired molecular property by interpolation (or extrapolation) from the known properties of their neighbors and to assist in the compression and computerization of immense quantities of data. (ii) An educational goal: the possibility of discovering qualitative chemical trends of molecules directly from a molecular chart. (iii) A philosophical objective: to seek yet another illustration that the whole is larger than the sum of its parts. A molecule is not the arithmetic sum of its atoms; although a large number of molecular properties can be treated as additive, many are not. (iv) A psychological reason based on scientific and human curiosity: why not try?

4.1.4 Atomic Periodicity Versus Molecular

Another related question is whether it is necessary at all to separate molecular

periodicity from atomic periodicity. Although the periodic law was formulated to be equally valid for both elements *and their compounds*, the proof was actually limited to the series of binary compounds (e.g. the oxides, hydrides and halides) of a given row or column. In such simple cases molecular periodicity can definitely be reduced to the atomic case, a viewpoint often reflected in chemistry textbooks. This approach, however, immediately fails if one looks at the relation between different classes of binary compounds (e.g. NaCl and CaO), or between binary and ternary compounds (e.g. NaCl and K_2SO_4), or between an inorganic and an organic substance. For such cases molecular periodicity, if shown to exist, may be only indirectly connected with atomic periodicity (or not follow from it at all). Hence, an alternative methodology, capable of comparing any pair of molecules, is required.

4.2 Problems with Global Classification and their Avoidance

4.2.1 The Infinity Problem

The first serious problem directly associated with the idea of molecular periodicity is the infinity problem. Indeed, in contrast to the *finite number of atoms* (about 100), the number of possible molecules constructed from them is actually infinite, and hence we can never construct a wall-chart for all molecules, since there is *no infinite wall*. (Of course, this assertion assumes that there is no limit to the numbers of atoms which we can imagine to be in molecules!)

How can the problem of infinity be resolved? We see two possible solutions: to separate the infinity into finite sets (of which there will be an infinite number) or to separate the infinity into 'smaller' infinities (of which there will be a finite or infinite number).

Infinite number of finite sets. The number of all imaginable molecules is infinite, but the number of diatomic or triatomic molecules is finite. The same is true for any case when the number of atoms in the molecules is fixed. So, a global classification can be considered as a step-by-step constructing of the local systems of N-atomic molecules and some comparisons of such systems. Analogously, we can separate infinite sets of molecules into (say) finite subsets of isovalence-electronic or iso-inner-electronic molecules.

'Smaller infinities'. Let us take a familiar example from mathematics: the infinite set of natural numbers can be separated to subsets of odd and even numbers. In such a case one infinity breaks down into two infinities, each with special peculiarities. Similarly, we can develop some finite or infinite number of important features to separate one infinite class of molecules from another. A good example from chemistry is the separation of the hydrocarbons C_nH_{2n+x} according to the saturation degree x (as in the Beilstein handbook). Another example is the classification of planar cyclic delocalized systems according to the Hückel rule⁶¹ ($4n$ or $4n + 2$ π -electrons). Analogously, the boron hydrides (boranes) and carboranes can be arranged according to Wade's electron counting rules of $(n+k)$ -electrons.⁶² Of course, these rules are valid only for certain local classifications; analogous rules for

global classifications still need to be developed.

4.2.2 The Multidimensionality Problem

Theoretically, we can imagine one classification of molecules as a hyperspace in which the number of axes is equal to the number of elements, and where the calibrations on the axes will be the numbers of the appropriate atoms in the molecule. (Thus, Decker's system for hydrocarbons⁵⁶ will be a plane in this hyperspace.) However, this classification results in a complete loss of visual clarity and is therefore unacceptable. The human eye is able to perceive only two-dimensional or three-dimensional pictures and, therefore, any attempt to compare molecules by such pictures may lead to degeneracies. In such a situation it is a requirement that any molecular 'chart' be as instructive as possible. Development of computer software opens new horizons for perceiving and manipulating objects in multidimensional spaces, and this may turn out to be the most promising way to resolve the problem of many dimensions.

4.2.3 The Polymorphism Problem

Seeking for a natural system of molecules can be considered as a search for a finite set of natural descriptors, capable of distinguishing between any pair of molecules. Evidently, such descriptors should be capable not only of distinguishing the molecules of different constitution, but also of discriminating among the isomers of a given formula. It should be mentioned, however, that the isomerism phenomenon in chemistry is the worst case of polymorphism of natural objects. Indeed, the vast growth in the number of isomers with an increase of number of atoms in organic molecules is well known (the combinatorial explosion).^{36,63} Thus, the hydrocarbon $C_{30}H_{62}$ has 4,111,846,763 isomers (see, e.g.,^{36b}). Another aspect of this problem is the polymorphism (using the word in a most general sense) of isomer types.^{36,37} Examples of such types are alternative arrangements of atoms in the skeleton (as in HCNO and HNCO), topological differences of structures (as in the cyclic and acyclic structures of O_3 and as in the differently branched skeletons of butane and iso-butane), differences in geometry (as in cis- and trans-, and syn- and anti-isomers), conformation (as in rotamers), and chirality (as in enantiomers).

In spite of some pessimism caused by such a gloomy succession of polymorphism problems, modern chemistry has developed various approaches and techniques in order to distinguish isomers of different types. Let us consider only one illustrative example: how to distinguish by natural numbers two isomers with a different 'degree of branching' – butane and isobutane. A very crude image of a molecule is its presentation as a set of atoms and 'rubber' bonds. More strictly speaking, skeletal structures of molecules can be represented by graphs – mathematical objects that are sets of points (vertices) connected together by lines (edges).⁶³ Atoms of a molecule can be naturally associated with the vertices, and the bonds with the edges, of a graph. In mathematical chemistry, molecular structures are often presented without terminal hydrogen atoms as so-called 'hydrogen-suppressed graphs'. Such graphs for butane and isobutane structures are

presented in Figures 13a,b. These two structures can easily be distinguished from one

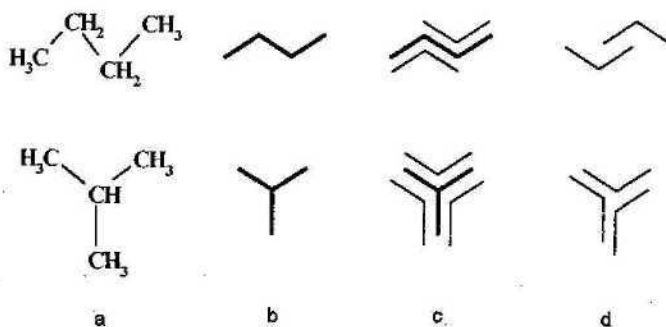


Figure 13 Distinguishing between butane isomers. Initial structures (a) are changed to their hydrogen-suppressed graphs (b). The latter are compared with the graph of propane in (c). The number of propane fragments found in the isomers is different, (d).

another by comparing them with the graph of propane – the previous member of the homologous series (Figure 13c). One can conclude that the structure of propane can be found twice in the structure of butane, and three times in the structure of isobutane (Figure 13d). These numbers – 2 and 3 – can be considered as the simplest numerical parameters (topological indices) that distinguish the two isomers.

Such topological indices can be defined in quite different ways; they may then have more or less discriminative power, and they may correlate with different physical properties of molecules.^{36,63} It is also true that various combinations of different indices can be used. A discipline that studies this area – the Quantitative Structure-Property Relationship (or QSPR) approach – is now a rapidly developing branch of chemistry.^{64,65} Methods have recently been put forward in this field that are directed at distinguishing between geometrical isomers. We have given special attention to this aspect of isomerism in order to emphasize that at least one of the above mentioned problems of global polymorphism may be avoided.

Finally, we conclude by observing that the paradigm of global periodicity is not entirely hopeless. The history of chemistry is full of intriguing empirical observations and generalizations that may help us to avoid the problems discussed above. Moreover, as we shall show later, chemists do have tools not only for natural distinguishing of dissimilar structures, but also for the natural ordering of chemically similar molecules.

4.3 Choice of Global Similarity Parameters: Importance of the Electron Count

Any classification implies an arrangement of objects into classes according to their similarities and dissimilarities. The problem of similarity in chemistry has attracted special attention in the past decade, and a classic book⁶⁵ discusses different aspects of this problem. Of course, any qualitative conclusion on the similarity or dissimilarity of two molecules might be arbitrary, though chemists have discovered

some parameters that are of major importance for molecular similarity studies.

In an effort to determine useful parameters for molecular classification, it might seem reasonable to assume that the origin of molecular similarity lies in atomic similarity. As we discussed above, any atom has two invariants responsible for its similarity with other atoms. These are its column (group) number and its row (period) number, and these two numbers reflect the numbers of valence and inner electrons in the atom. Modern molecular orbital theory treats molecules somewhat analogously to atoms; it also separates the electrons in a molecule into valence and core electrons. These two key atomic invariants – the number of valence and of inner electrons, therefore, can be considered as transferable parameters applicable both to atoms and molecules. Consequently, the total number of valence electrons (Z_v) and the total of inner electrons (Z_i) of molecules could serve as promising parameters to establish molecular kinship. The number of atoms (N) in the molecule is another important and simple parameter.

'Vertical' isovalency. The isovalency of atoms of the same group often causes structural and chemical similarity in a series of related molecules formed from them. Thus the series of the halides in group five – binary compounds (such as NF_3 , NCl_3 , PF_3 , PCl_3) or mixed derivatives (such as NF_2Cl , PFCl_2 , PFCIBr) – are isovalent and differ only in their inner shells. In such cases the entire family of molecules can be represented by its *isovalence type* by simply changing the atomic symbols to the appropriate number for the group of elements in the periodic table. In the examples of fifth-group halides just discussed, $Z_v = 26 = 5 + 7 + 7 + 7$ and the isovalence type (which is actually the 'chemical formula' of the entire class) is 5777 or 5(7)₃.

'Horizontal' isovalency. The isovalency of molecules may arise not only from the 'vertical isovalency' of atoms in groups of the periodic chart, but also from the 'horizontal isovalency' of atoms and corresponding ions from the same row. The general rule is that similar substitutions in the isovalent series provide isostructural molecules. Thus, we can take the series of ions Be^{2+} , B^{3+} , C^{4+} , N^{5+} (isoelectronic with the helium atom) and add a fixed number of ligands such as H^- or F^- . In this manner the structurally similar families of tetrahedral hydrides (BeH_4^{2-} , BH_4^- , CH_4 , NH_4^+) or fluorides (BeF_4^{2-} , BF_4^- , CF_4 , NF_4^+) may be obtained. Analogously, we could use different ligands (e.g. nitrogen, as in the linear anions NBN^{3-} , NCN^{2-} , NNN^- or oxygen, as in the triangular anions BO_3^{3-} , CO_3^{2-} , NO_3^-). We can also start from another series of ions (e.g. ions C^{4-} , N^{3-} , O^{2-} that are isoelectronic with Ne and give pyramidal structures CH_3^- , NH_3 , H_3O^+ with a proton as the ligand) to yield ever more new series of isostructural molecules.

Comparing the structures of isoelectronic molecules obtained from 'horizontally isoelectronic' ions (as in the examples above), one can conclude that their difference can be alternatively considered as the result of an imaginary addition (or removal) of a proton from the nucleus of the central atom of the molecule. Thus, we can view the series BO_2^- , CO_2 , NO_2^+ as the result of the addition (removal) of a proton to (from) the central carbon atom of CO_2 rather than as the result of addition of two O^{2-}

ligands to the isoelectronic ions B^{3+} , C^{4+} , N^{5+} . (Long ago Bent, having reviewed many such series, proposed the apt term 'alchemical' for such imaginary proton shifts.⁶⁶) This idea can be generalized and applied also to the ligands or, broadly speaking, to any heavy (non-hydrogen) atoms of more complicated structures. Thus, we can get the linear ions ONO^+ and NNN^- by such addition (removal) of a proton to (from) terminal ligands of the linear molecule NNO or obtain the hexagonal pyridinium cation from benzene.

Isosterism. Perhaps the most intriguing and surprising result is that molecular similarity appears not only via imaginary additions or removals of protons, but also in the mental 'internuclear rearrangements' of protons between the heavy nuclei of the same molecule. Thus, a consistent shift of protons among the heavy atoms of NNO leads to the isostructural family of linear OCO , FCN , FBO , $FBeF$ molecules. This phenomenon – called isosterism – was first described in the 1920s by Langmuir,⁶⁷ who observed pronounced similarity in the macroscopic properties of CO and N_2 , and of NNO and CO_2 ; another frequently cited pair of isosteres is benzene and borazene, again with very close physical properties. The isosterism principle has proved its usefulness both in chemical education and in the practical search for novel classes of molecules.⁶⁶⁻⁶⁸ Isosterism is considered to be responsible for the isomorphism of crystals, the constitution of alloys (Hume-Rothery's phases) and the similarity in spectra of isoelectronic molecules.

Protonation and/or deprotonation. The cited examples underline the unique role of the proton in deciding on the similarity between molecules of different constitution. Unlike other particles, the proton has two symbols (p or H^+), indicating that it is simultaneously an elementary particle of physics (symbol p) and an important 'molecule' of chemistry (symbol H^+), responsible for the usual acid-base properties of chemical compounds. A well-known chemical characteristic of the proton is that its addition or removal as a ligand (as in acid-base processes) again only slightly perturbs the initial molecular structure. Indeed, the molecule of ammonia NH_3 (which is almost tetrahedral with one vertex occupied by a lone pair) can be protonated (to form tetrahedral NH_4^+) or deprotonated (to form the amide anion NH_2^- , a tetrahedron with two vertices occupied by lone pairs) with approximate conservation of initial structure. Exceptions appear only if there is another driving force (such as delocalization or aromaticity) that tends to change the geometry of charged species. Analogously, tautomerism – the chemical shift of a proton from one heavy atom to another in such a way as to leave the atomic census unchanged (as in $HNCO$ and $HOCN$ or in the C- and O-forms of the acetoacetic ester) – in most cases conserves the initial skeletal geometry of the molecules.

Grimm series. Invariance of the structures of isoelectronic molecules toward both imaginary and actual proton shifts can be also illustrated by the superposition of such shifts. Grimm in the 1920s first drew attention to the fact that structural similarity of molecules exists in the special isoelectronic series that have hydrogen as the variable

atom.⁶⁹ Grimm illustrated his 'hydrogen displacement principle' by considering both neutral molecules (e.g. Ne, HF, H₂O, NH₃, CH₄) and radicals or functional groups (e.g. Cl, SH, PH₂, SiH₃). (It is interesting that in the 1930s there was a sharp controversy (see refs. 58b, 58c) between Shemyakin and Grimm over credit for the discovery of this 'hydrogen displacement'; Shemyakin considered this principle as a particular case of his nine tables, see above.)

Evidently the relationship in the Grimm series is the consequence (or superposition) of imaginery ('alchemical') and chemical proton shifts. For example, in the simplest pair (Ne → HF), the proton is (i) taken from the nucleus of a heavy atom as the 'physical' particle (Ne → F⁻ + p), then (ii) is reconsidered as the 'chemical' particle (p=H⁺), and (iii) is retained as a ligand by formal protonation of the anion F⁻. This procedure is equally applicable to molecules with one or more heavy atoms (cf. the relationship between the structures O=C=O, HN=C=O, H₂C=C=O, and H₂C=C=CH₂ or between isobutene and F₂C=O).

It should be emphasized that the local environment of a heavy atom in a molecule appears to be almost insensitive to the chemical and imaginery addition or removal of protons. As a result, the entire molecular skeleton around heavy atoms also remains almost unchanged toward such proton shifts, as well as toward internuclear (isosterism) or intramolecular (tautomerism) rearrangements of protons. Since the proton is a unique chemical particle bearing no electrons, the invariance of the electron number may be considered as the parameter responsible for the skeletal similarity of isovalent families. These early conclusions, later intensively and extensively studied in different fields of inorganic and organic chemistry, have been met with a rather limited number of counterexamples. For the quantum-chemical aspect of the problem and analysis of the known exceptions, see, e.g., the review in ref. 70. Isovalency, therefore, can be treated as a generalization of elements' similarity in groups that is quite naturally applicable to molecules.

5. The Art and Logic of Equalization: Classification of Isosteric Ensembles

5.1 General Remarks

Surprisingly enough, the isovalency principle has usually been applied only to local classifications of molecules. How can the principle be used with respect to global molecular periodicity? The early Renaissance philosopher Nicolaus von Kues (Cusanus) said⁷¹ 'equality foregoes inequality.' Let us take this expression as our motto and declare *all* molecules with equal numbers of valence electrons Z_v to be *equal objects*. Of course, we ignore any differences between the isomers, isosteres, and molecules differing by the chemical and 'alchemical' (see Section IV.3) shifts of protons. As we mentioned above, in many cases there are very good chemical reasons why we are able to neglect such differences.

By definition we neglect any difference in the inner shells, and consider as equals the members of such sets as Li₂O and Cs₂S, and F₂, I₂ and BrCl. This procedure is somewhat similar to approximating the entire periodic chart of elements by only one of its periods, say the one that contains the elements from Li to Ne. This approximation makes sense only if elements from the main groups are considered;

hence we also limit ourselves to molecules constructed from atoms of the main groups. Having arranged all molecules into isovalent series, we may order the series by increasing the Z_v value. Actually, in this way, we project a multidimensional space of all molecules on to one-dimensional space or a line.

Of course, the number of valence electrons has rather poor discriminative power. The degree of degeneracy (or polymorphism), that is the number of molecules with the same Z_v , quickly increases with increasing of Z_v . However, we may ask: what is the extent of this degeneracy, and how many neutral molecules are theoretically possible for a given Z_v ? To avoid the complexity of isomerism, let us ignore it, and simplify the question thus: how many different molecular formulas are possible for a given Z_v ? The question is still ill-defined, since the total of valence electrons does not reflect the exact formulas but rather symbolic 'valence formulas', which we called isoelectronic types. So, the only question we can ask is: how many isoelectronic types exist for a given Z_v ?

The answer exists, and follows from the mathematical theory of numbers: the number of isoelectronic types associated with any given Z_v electrons is equal to the number of partitions of the number Z_v . The partition of a number Z_v is any unordered sequence of numbers whose sum is equal to Z_v ; thus (2,2) is a partition of 4 since $2 + 2 = 4$, and (3,1) or (1,3) are also partitions of 4 for the same reason. There are only 5 distinct partitions of $Z_v = 4$, and these partitions are (1,1,1,1), (2,1,1), (3,1), (2,2), and (4). Therefore, there are exactly 5 isoelectronic types of neutral molecules with 4 valence electrons. Since we identify the size of any part of the partition as the group number of a main-group atom, it follows that the parts of a partition have *limited size*, up to eight.

The numbers of partitions (i.e. isoelectronic types) for the first seven Z_v are as follows:

Z_v :	1	2	3	4	5	6	7
No. of partitions:	1	2	3	5	7	11	15

General formulas to calculate the number of partitions are rather complicated, but they do exist;⁷² for specific cases one may calculate by hand or use a simple computer program. In any case, the existence of a means to calculate the number of isoelectronic types (partitions) as a function of Z_v is very important. Its importance lies in that, now, the problem of polymorphism (at least in respect to one of its possible types) can be treated in a purely combinatorial sense. (Earlier, when we deliberately admitted polymorphism into our classification, we had absolutely no quantitative idea about the nature and degree of this polymorphism.)

Let us consider the additional and quite natural parameter, the number of atoms N in the molecule. We can use it as the second axis, making our global classification into a two-dimensional projection of a system of all molecules on the coordinate plane (Z_v, N). Every point on this plane contains a certain finite set of (isovalent) neutral molecules with a fixed number of atoms, i.e. isosteres. Let us call such sets

isosteric ensembles, and call the entire plane the Plane of Isosteric Ensembles.

The coordinates of isosteric ensembles in the Plane of Isosteric Ensembles lie within boundaries. Thus, when increasing the number N along isovalent series with a given Z_v , we 'crush' larger parts into smaller parts. The maximum extent of this crushing is an association of N protons (or alkali metals each with one valence electron) and hence the maximum N for a given Z_v is $N = Z_v$. Analogously, being limited by a maximum of eight valence electrons of any (main group) atom in the molecule, we cannot have in an N -atomic molecule more than $8N$ electrons (as in an association of N noble gas atoms), so the maximum Z_v for a given N is $8N$. Consequently, all points of the (Z_v, N) plane fall inside the sector bounded by lines $N = Z_v$ and $N = 1/8 Z_v$. Evidently, any line parallel to one of the coordinate axes (i.e. isovalent and isoatomic families) should cross the region between these boundary lines (Figure 14). The periodic table on this chart is simply the line $N = 1$ with eight points.

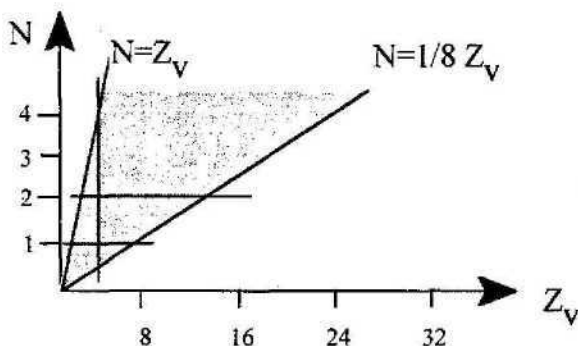


Figure 14 A possible arrangement of isosteric ensembles on the Plane of Isosteric Ensembles (shown by the gray area).

Since chemists consider the grouping of molecules into isosteric families to be quite reasonable, the question arises as to the similarity and dissimilarity relationships *between* isosteric ensembles. The Plane of Isosteric Ensembles (first introduced by one of us in the 1980s^{50,51}) seems to be just the answer needed to this question. As we shall prove below, the Plane of Isosteric Ensembles is an important pattern for molecular classification, since it (i) possesses a unique symmetrical structure with respect to polymorphism, (ii) may be used for a qualitative dichotomy of molecular chemical types, (iii) reflects key topological trends of molecular structures, and (iv) obeys a kind of periodic law quite different from that of atoms: we shall call it the law of 'hyperperiodicity'. In other words, the Plane of Isosteric Ensembles (in spite of its seeming simplicity) may serve as a source of *novel knowledge* about molecular periodicity.

5.2 Regularities in the Polymorphism of Isosteric Ensembles

The first problem appearing in the model based on the Plane of Isosteric Ensembles

is the polymorphism of isosteric types. Every isosteric ensemble has a different 'capacity' owing to the different number of theoretically possible isosteric types (i.e. partitions). Let us estimate, at least qualitatively, how this capacity varies, say along the N -atomic series. In a diatomic series, for instance, with an increase of Z_v this capacity first increases and then decreases. Thus, for $Z_v = 2, 4, 6, 8, 10, 12, 14$ and 16 , the capacities (i.e. number of partitions into two parts each no larger than 8) are $1, 2, 3, 4, 4, 3, 2$ and 1 , respectively. These numbers of partitions are plotted perpendicular to the Z_v, N plane in Figure 15.

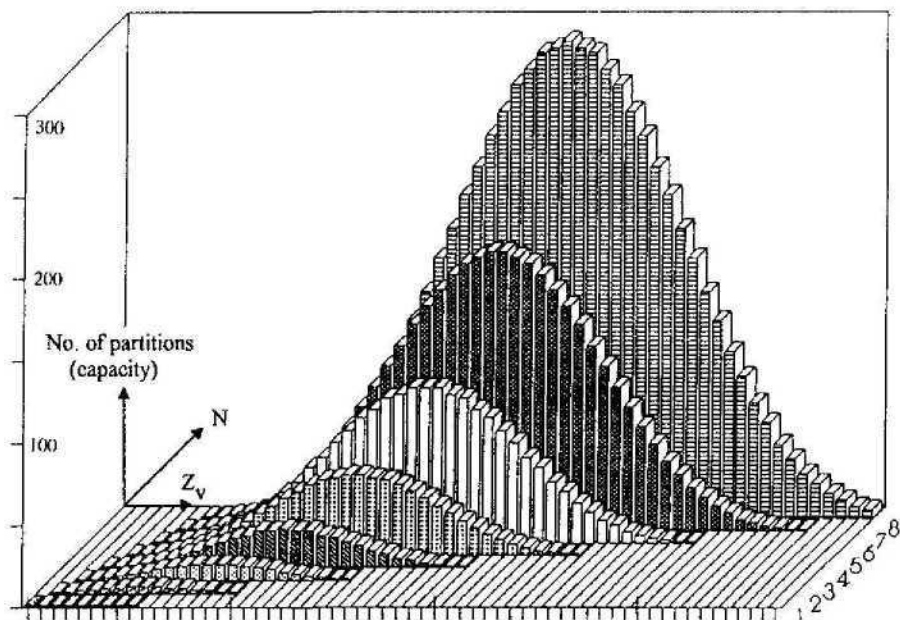


Figure 15 Regularities in the capacity of the isosteric ensembles along N -atomic series. (The number of partitions is plotted against the (Z_v, N) plane.)

The result is remarkable: the capacity along *any* isoatomic series is symmetrical and is represented by a Gaussian-like curve. This peculiarity follows from the combinatorial properties of partitions with parts of a limited size. The proof can be found in any elementary course in partition theory (e.g. ref. 72).

This observation gives us at least two advantages. The first is that the degree of polymorphism is small (and may even be neglected) for molecules at the beginning and at the end of any isoatomic series; thus the discriminative power of Z_v and N is enough for such particular cases. The second is that polymorphism itself (at least, with respect to the number of isosteres) appears to be a periodic-like phenomenon.

5.3 Chemical Trends: the Rule of Two Poles

Since the time of Plato and Aristotle scientists have spoken about the objects of the universe in terms of binary opposites. In the chemical tradition opposites are also

widely used, and one can easily recall such archetypal opposites such as:

- (a) metals and non-metals,
- (b) reductants and oxidants,
- (c) acids and bases,
- (d) electrophiles and nucleophiles, and even
- (e) organic and inorganic compounds.

The first opposite (a) is related to the elements, while the other opposites (b), (c), (d), and (e) are, of course, related to molecules and compounds rather than atoms and elements. The opposite 'metals - non-metals' for elements is connected with their disposition in the periodic chart (locations in the lower-left and upper-right corners of the table, respectively). Is it possible to treat opposites from (b) to (e) among molecules in relation to the dispositions of their isosteric ensembles in the Plane of Isosteric Ensembles? Let us look at the Plane in a new way by placing on it concrete examples of chemical formulas instead of partition symbols (Figure 16).

Even a quick review of the molecules arranged on the Plane of Isosteric Ensembles gives an intuitively clear picture. On and near the lower-right boundary of the Plane there are typical inorganic molecules with pronounced acidic properties, strong oxidants, and/or powerful electrophiles. The upper-left region of the Plane, on the contrary, is occupied by typical organic and organometallic molecules that are reductants, strong bases, and/or nucleophiles. In other words, the key chemical opposites (b), (c), (d), and (e) appear at different portions (or 'poles') on the plane, the first being located near the boundary line $N = 1/8 Z_v$, and the second close to the boundary $N = Z_v$. How can this 'two poles rule' be explained?

In order to prove that the observed duality is neither artificial nor accidental, let us check the behavior of any partition with respect to variation of the N and Z_v values in the direction of both poles. It will be helpful to change the numerical presentation of each partition to its equivalent pictorial form (known as Ferrer graphs in mathematics and as Young diagrams in physics).⁷² The pictorial presentation simply matches the size of every part in a partition by a set of points (squares) arranged horizontally (size of parts) and vertically (number of parts), Figure 17 (left). The number of squares in a row is equal to the numerical value of the part, and the number of rows is equal to the number of parts in the partition.

As one may easily see in the right side of Figure 17, any shift down or to the right necessarily causes an *increase* in the size of at least one part in the partition. Conversely, every shift up or to the left always *decreases* the size of at least one of the partition's parts. However, the size of a part is the atom's group number. The atom's group number, in turn, reflects the element's electronegativity. Hence, the upper-left part of the Plane of Isosteric Ensembles is populated with molecules from electropositive atoms (smaller group numbers), and the lower-right part is populated by molecules from electronegative atoms. Consequently, the dichotomy which we noted on the Plane has a natural origin and can be explained by the use of partitions and their relation to the electronegativities of atoms in molecules.

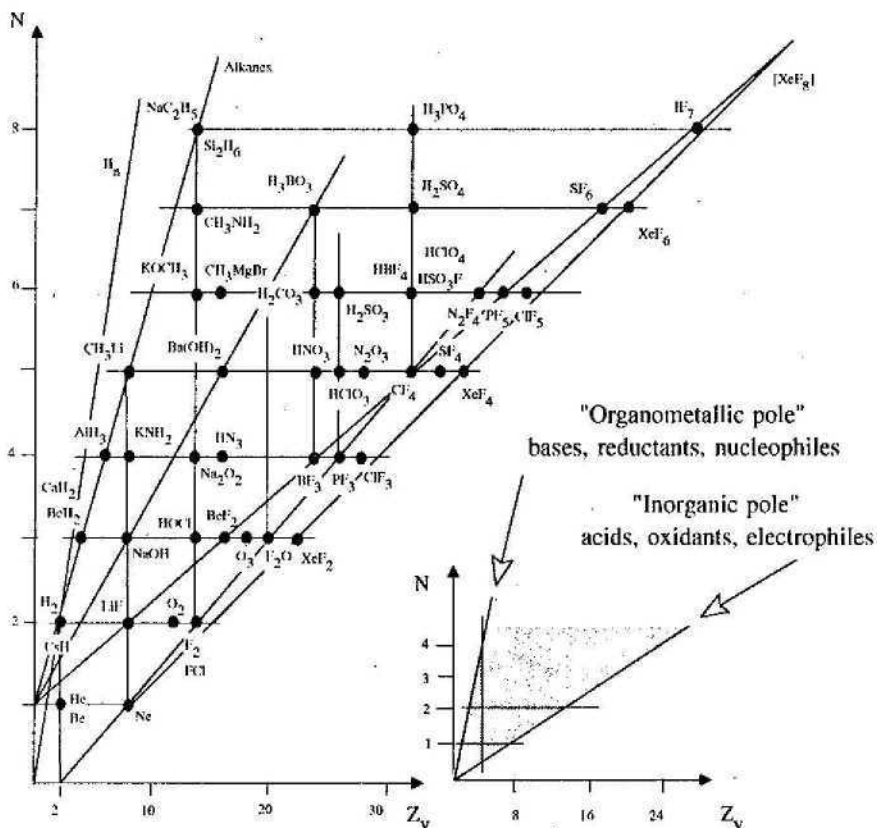


Figure 16 Arrangement of concrete molecules on the Plane of Isosteric Ensembles and symbolic presentation of two chemical 'poles' at the boundaries of the Plane. (Adapted from ref. 50.)

Theory of Numbers and Chemistry: More Interactions?

We may talk about the two poles in another manner. Consider a diagonal line on the (Z_v, N) Plane that starts from the origin. We may continuously vary the slope of this line, thus covering any point on the plane. The variable parameter of the slope may be simply the cotangent of this line, that is, the ratio Z_v/N (i.e. the relative number of valence electrons per atom). Small values of this electron-to-atom ratio correspond to the organometallic pole, while large ratios (up to 8) correspond to the inorganic pole. This ratio, of course, is insensitive to the extent of self-association, (i.e. it does not distinguish between ethylene and polyethylene, or between diatomic NaCl and hypercluster $[\text{NaCl}]_x$), and therefore it is one more useful classification parameter.

This ratio is especially useful for classifying different homological series where the members differ by the same group (a group like CH_2 , phenylene, HPO_3 , etc.).

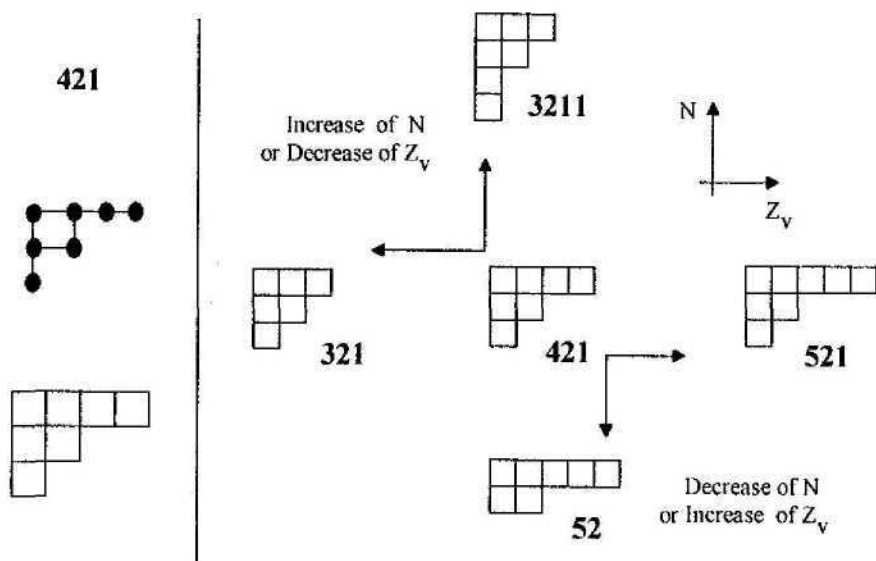


Figure 17 *Left:* Graphical presentation of a partition by a Ferrer graph and a Young diagram. *Right:* The 'two poles rule' as the specific property of partitions. (Taken from ref. 51.)

Indeed, if the same group is introduced many times, then the value of Z_v/N approaches as a limit the ratio of the inserted group. Thus, ratios for very long (polyethylene-like) CH_2 -homologs of NH_3 and HCl converge to the ratio of the CH_2 -group. Generally, the value Z_v/N is a rational number, but sometimes it is a natural number (like 4 in the polyacetylenes, 3 in sugars differing by a $-\text{CH}(\text{OH})-$ group, 2 in the usual $-\text{CH}_2-$ homologs, and 1 in hydrogenated series such as alkyne-alkene-alkane.)

The great mathematician Felix Klein once stressed⁷³ that a line on a plane (with natural numbers as calibrations on the axis X and Y) is the best illustration of the difference between *rational* and *irrational* numbers. (Examples of irrational numbers are square roots of some natural numbers, the Fibonacci number, or the number π .) Indeed, the cotangent representing the slope of a line from the origin which meets any point of such a plane is a rational number (obviously so if the point has integers X and Y). However, on such a plane a line with an *irrational* cotangent *never* meets a point; and vice versa, no point will ever be found on such a line.

In respect of the isosteric ensembles on the (Z_v, N) plane, it is an intriguing question whether the electron-to-atom ratio Z_v/N may ever be an *irrational number*. The reason for this question is that the well-known Hume-Rothery phases tend to have an electron-to-atom ratio of $21/13$, as if they were on an imaginary line with the irrational Fibonacci number as the cotangent. Analogously, the simplest oligopeptides have an electron-to-atom ratio surprisingly close to the number π . The ratio $22/7$ for $-\text{NHCH}_2\text{CO}-$ of glycine is the first known rational approximation for

π ; the next approximation to π requires at least four such groups. Did nature provide the flexible set of 20 or so natural amino acids just in order to express its primordial irrationality? Of course, care should be taken with such 'chemical numerology', but there is another large area – the bertholides that are not daltonides – where such thinking could be important.

5.4 Distinguishing between Molecules in the Plane of Isosteric Ensembles

The molecules we have declared equal actually are not, and we called this polymorphism. The problem is how to avoid this polymorphism and better distinguish the molecules in an isosteric ensemble. Should we add only one or more axes to the Plane of Isosteric Ensembles? Which distinguishing parameters are the natural ones, and are they useful for further natural classifications? We may call the problem of distinguishing neutral molecules on the Plane of Isosteric Ensembles 'the three i problem'. The three i problem is that isosteres, isomers, and inner-shell-differentiated molecules (vertically isovalent molecules) are not distinguished.

1. Isosteres. Let us take first isosterism: what are the actual differences between the isosteres that should be reflected by a distinguishing parameter? Consider examples of isosteric families, say (LiF, BeO, BN, CC) or (NNO, OCO, FCN, FBO, FBcF). It is clear that in an ensemble the difference is in the polarity of bonds, which in turn follows from the degree of homogeneity or heterogeneity of the entire molecule. Since we have approximated the set of isosteric types by partitions, how can the 'homogeneity' of partitions be expressed? The simplest way is to calculate differences in the size of parts of partitions, and this is the best distinguishing parameter for diatomics. Indeed, such differences for the series (1,7), (2,6), (3,5), (4,4) are respectively 6, 4, 2, 0 and reflect an evident difference in the polarity of the bonds (say, in the above family LiF, BeO, BN, CC).

Unfortunately, the set of such binary differences appears with an increase of the number of atoms, and it is unclear how to describe such 'homogeneity' even for triatomics. (The sum of differences leads to degeneracy; thus the partitions (4,4,1) and (5,2,2) have the same set of differences 0, 3, and 3.) One alternative way is to write the numbers of every partition in decreasing order, e.g. (5,1,1), (4,2,1), (3,3,1), (3,2,2), and to sort the partitions according to decreasing magnitudes of the larger numbers. We consider this problem of how best to distinguish partitions to be still open. If this parameter is defined as a number, we can imagine a third axis to our plane. This axis brings one new *binary opposite*: between ionic (polar) and covalent (non-polar) molecules.

2. 'Vertically isovalent' molecules. We wish to emphasize that the Plane of Isosteric Ensembles is a periodic system by definition. Indeed, all the chemical trends of the isosteric ensembles discussed above with respect to their arrangement on the plane (Z_v, N) are connected only with valence electrons. Hence, we can add one more axis – a parameter sensitive to the number of inner shells (or inner electrons) – thus obtaining many such planes. This axis should distinguish between

light and heavy molecules, and it may also bring more opposites related, say, to the concept of hard and soft acids and bases.

The question is how to realize such discrimination in practice. Consider, for example, the entire family of the fourth group halides (CBr_4 , SiF_2Cl_2 , CF_3I etc.) represented by the same partition (4,7,7,7,7). The seemingly obvious advice – to take the total sum of the inner-shell electrons – fails, due to possible degeneracy (like $2 + 18 = 10 + 10$); the same is true for period numbers ($4 + 3 = 5 + 2$).^{43,50} How this problem can be resolved for the simplest case of diatomics is discussed below (Section 7).

3. Isomers. Now we return to the problem of distinguishing isomers. As mentioned in Section 4.2, the entire area is quickly developing. However, the problem of rational discrimination of *any* given pair of isomers is still open. Let us suppose that an ideal super-discriminative index for isomers exists (or will be proposed in the future). If the index is a number, then the isomers will be discriminated by one more axis. What exactly will be discriminated (say, degree of branching or symmetry), and hence what opposite will appear, will be determined by the nature of the parameter.

So, it seems that ideally (to get a complete resolution of the ‘three i problem’) we need three more independent axes ‘perpendicular’ to our Plane of Isosteric Ensembles, i.e. some sort of space with five dimensions. The problem is complicated by the fact that we have ignored transition and rare-earth elements for which it may be necessary to add one or more parameters (see Section 7). Until this space is constructed, we shall continue to learn more from its simplified two-dimensional projection – the Plane of Isosteric Ensembles.

5.5 Topological Trends in the Plane of Isosteric Ensembles

Next, the question arises: is it possible to reflect in any way the structural trends of molecules, starting only from the model and using the Plane of Isosteric Ensembles without the addition of new coordinates to that two-dimensional plane? What can we learn about molecular structure simply from counting the valence electrons and the atoms?

5.5.1 Point on the Plane of Isosteric Ensembles as a Set of Molecular Pseudographs

We may try to relate Z_v to the number of bonds. The crudest assumption is that any chemical bond is localized and corresponds to a shared pair of valence electrons. In such an approximation chemistry is related to graph theory as follows:^{63,74} atoms correspond to the vertices, and bonds correspond to the edges, of a graph (see Section 4.2). There is no problem in imagining bent multiple edges between a pair of vertices, representing familiar double or triple chemical bonds. However, the total sum of two-electron bonds multiplied by two is not equal to the total of valence electrons Z_v : some electron pairs may turn out to be the non-bonding lone pairs that are drawn in classical Lewis diagrams as pairs of dots. But how does one express

lone pairs in a graph?

The simple answer often discussed in the literature is to use loops, i.e. bent edges of a graph that start and finish at the same vertex. Graphs with such loops are called pseudographs.⁷⁴ Any vertex of a (pseudo)graph is characterized by its degree – the number of edges adjacent to this vertex. If we consider that the two ends of a loop add 2 to the vertex degree, then a molecular pseudograph has an elegant feature: the degree of any vertex is simply the group number of the matching atom in the (main-group part of) the Periodic Table, see Figure 18. Hence, the total number of vertices (V) exactly corresponds to the number of atoms ($V = N$), and the sum of all edges (E) is half the number of valence electrons ($E = 1/2 Z_v$) in the corresponding molecule.

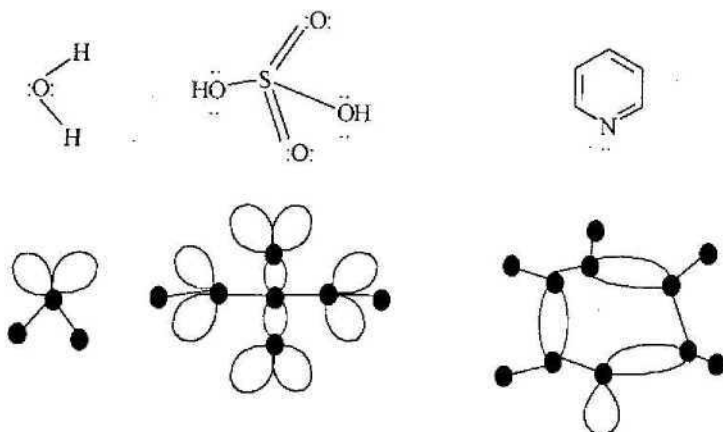


Figure 18 Examples of the pseudographs for molecules of water, sulfuric acid, and pyridine.

Evidently this discussion makes sense only for molecules with an even value of Z_v and, among this class, only for molecules with closed shells (that are not biradicals). For them, we may conclude that every point Z_v on the Plane of Isosteric Ensembles corresponds to a set of pseudographs with the same number of edges (E) and the same number of vertices (V). Hence, we may redraw the Plane on new axes E and V , and place on it some examples of pseudographs (Figure 19). What can be learned from such a presentation?

5.5.2 Counting of Cycles and Components from Electrons and Atoms

A pseudograph may either be connected or not, i.e. it may consist of K parts or components. The parameter K can be identified with the number of isolated molecules (say, as a molecular ensemble before or after a reaction). A pseudograph may consist of C cycles. The cycles can be of various sizes: thus, there may be the usual cycles of size 3 or higher (as in the cycloalkanes), and there may be less usual formal cycles of size 2 (as in double bonds) or even strange cycles of size 1 (loops).

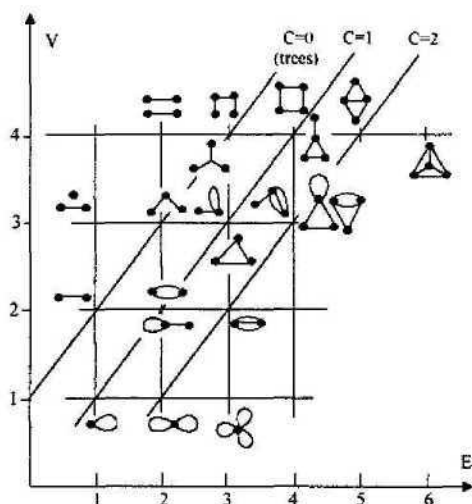


Figure 19 The Plane of Isosteric Ensembles redrawn as the (E, V) plane with examples of pseudographs. (Taken from ref. 50.)

The parameter C for molecules should be considered as the total number of molecular cycles, including the 'strange cycles'. The counting of cycles and components is a standard tool of topology, and the indices K and C reflect the simplest aspects of molecular topology. How do the values K and C follow from the valence electron count?

There is a well-known equation⁷⁴ that relates the total number of vertices (V), edges (E), cycles (C), and components (K) in a pseudograph (and any other graph); it is $V - E = K - C$. Consequently, for molecules with localized bonds, $2N - Z_v = 2K - 2C$. If only isolated molecules ($K = 1$) are considered, then 'isocyclic' molecules appear on the lines parallel to the bisector of the Plane of Isosteric Ensembles, i.e. to the line $V = E$ (or $N = 1/2 Z$), see Figure 19.

5.5.3 Cyclomatic Number of Pseudographs and Homeomorphism of Structures

More strictly speaking, the number C is the so-called cyclomatic number of the graph, i.e. the number of *independent* cycles.⁷⁴ For instance, in the graph of a tetrahedron (with solid vertices and edges but empty faces) only three cycles are independent; the fourth 'phantom-cycle' appears as the apparent result of the adjacency of three other cycles. If we cut edges (without forming new components), the independent cycles should disappear, and the final result of such cuts is a graph without cycles. Such a graph is called a tree. The cyclomatic number is the number of these cuts necessary to obtain a tree. Only three (not four) such cuts are necessary to destroy all the cycles in a tetrahedron and obtain a tree.

We may clarify and prove the topological nature of cycles in a rather unusual manner: by mentally inflating a graph. Consider a graph to consist of rubber tubes

(edges) that are adjacent to one another and closed at the terminal vertices. Inflating of such tubes causes transformation of the graph to some closed two-dimensional surface, in three-dimensional space, having the properties of the classical objects of topology (such as a sphere or a torus). In topology, these surfaces are classified according to the number of handles (this peculiarity is also called the genus of the surfaces).⁷⁵ Two surfaces with the same number of handles are considered indistinguishable, topologically equivalent, or homeomorphic (like the coffee cup and doughnut) and may be transformed into one another by the operations of 'rubber geometry' – continuous deformations without cuts and gluing. The genus stays topologically invariant in such transformations.

In our inflating model every handle appears from a cycle. The cycles, in turn, originate from the total number of lone pairs, multiple bonds, and (independent) cycles of a molecule. In this way, the genus of such surfaces corresponding to molecular structures follows from the electron count.^{51,76}

Homeomorphic two-dimensional surfaces originate from molecules with isocyclic pseudographs; we call such molecules homeomorphic. The arrangement of homeomorphic families in the Plane of Isosteric Ensembles is shown in Figure 20a, and an example of how to attribute a two-dimensional surface to a molecule is presented in Figure 20b.

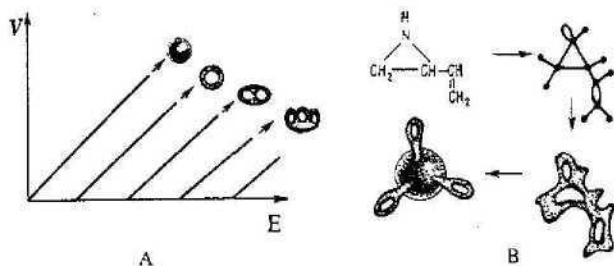


Figure 20 (a) Arrangement of homeomorphic families in the Plane of Isosteric Ensembles. (b) Steps from a molecule to its two-dimensional image via pseudograph. (Taken from ref. 51.)

What is the meaning of the genus (cyclomatic number) for molecules, and what does homeomorphism (or its absence) mean in molecular series? The simplest answer is that the genus is some sort of generalization of the usual degree of saturation in hydrocarbons. Let us explore the hydrocarbon case. Homological hydrocarbons of the formula C_nH_{2n+x} with given x have the same saturation degree x . For alkanes ($x = 2$) we have a sphere, for alkenes or cycloalkanes ($x = 0$) we have a torus. (Generally, x is the Euler characteristic of the surface.) Consequently, homeomorphism corresponds to the well-known phenomenon of homology for organic compounds. In many cases, homologs are rather similar in chemical

behavior, and their properties vary monotonically or sometimes even periodically.⁷⁷ Hydrocarbon homologs differ by CH_2 groups, and this group appears to be a unique one since its insertion does not change the C value (the cyclomatic number or the number of handles). Are there any examples of other groups with the same property?

There is another such fragment in the different context of aromatic cycles: the group CH^+ . One can easily see that this fragment is responsible for the difference between 5-, 6-, and 7-membered aromatic cycles with 6 π -electrons,⁶¹ namely the cyclopentadienyl-anion C_5H_5^- , benzene C_6H_6 , and the tropylium cation C_7H_7^+ . Hence, these chemically similar π -systems appear to be homeomorphic in the same sense that the usual CH_2 homologs are. Applying the 'alchemical' proton shift to the anion C_5H_5^- we obtain pyrrole, which is again homeomorphic to benzene. Of course, the homeomorphism caused by the insertion of a CH^+ group is not responsible for the origin of aromaticity. However, it conserves the initial aromatic (or anti-aromatic) pattern of a delocalized system.

One more example of a fragment that does not change the cyclomatic number is the group BH , isoelectronic with CH^+ . There is a well-known classification of the boron hydrides into the *closo*-, *nido*-, and *arachno*-families, according to the structural similarity of the molecules inside every series with the same 'homological difference' BH .^{62,78} Of course, we cannot attribute any pseudographs to such structures (their bonds are no longer localized). Nevertheless, if one plots the partitions for such families as points on the Plane of Isosteric Ensembles, the lines that are obtained will be parallel not only to one another, but also to the other lines of the usual CH_2 homological series.

We may conclude that the molecular cyclomatic number (or the genus of the appropriate two-dimensional surface) looks like a remarkable global index of molecular similarity that is insensitive to molecular dimension. Indeed, it is equally applicable to the similarities of chains (usual homology), polygons (aromaticity), and polyhedrons (clusters of boron hydrides). The generalization of this idea in respect to the rather intriguing topological conservation law in chemical reactions has recently been discussed by one of us.⁷⁶

5.5.4 Criteria of Connectedness for Molecular Pseudographs

Another topological property is the connectedness or disconnectedness of molecular pseudographs. Generally, connectedness is the ability to present an object as one piece rather than a few disjoint pieces (or components). Of course, making a decision about the connectedness of a molecule is necessarily arbitrary, since the nature of bonding between apparently disjoint pieces may vary dramatically (see, e.g., Grimm's tetrahedron, in Section 4.1.3). Nevertheless, it is possible to simplify the problem if we limit ourselves to molecules with localized bonds, constructed only from the atoms of the first two rows of the periodic table. It is easy to attribute a certain pseudograph to any such molecules (see the examples below) and consequently to compare their connectedness. Does connectedness relate to the arrangement of molecules in the Plane of Isosteric Ensembles? The answer is 'yes'.^{50,51} there are two regions in the Plane where molecules are *always*

disconnected (in the sense discussed above).

Loss of connectedness caused by electron deficiency. In Figure 19, isocyclic molecules lie on parallel lines. One such line ($V = E + 1$) consists of trees, i.e. molecular graphs without cycles. Examples of such molecules are LiH, BeH₂, BH₃, CH₄, C₂H₆ etc. Above and to the left of this line no connected graphs are possible at all, since there are not enough edges to connect the given number of vertices into a single entity. The molecules from this region (e.g. LiH₃ and C₂H₈) have electron deficiency, and hence it would be common sense to describe them as disconnected sets such as LiH + H₂ or CH₄ + CH₄ with localized bonds. We may change the terminology (by, say, counting bonding molecular orbitals instead of edges), but not the phenomenon (nor the existence of such a topological boundary). The consequence is that known molecules from this region (like boron hydrides or non-classical cations such as CH₅⁺) all have multicentered bonds.⁷⁹

Loss of connectedness caused by electron excess. There is another line in the Plane of Isosteric Ensembles, namely $V = 1/3 (E - 1)$, with the same simple property of being a topological boundary. This line corresponds to the series Ne, F₂, F₂O, NF₃, CF₄, C₂F₆ etc. Although there are loops in the pseudographs of these molecules, such structures are also 'trees' with respect to the number of bonds between the heavy atoms. Below and to the right of this line any molecular pseudograph appears to be always disconnected, otherwise it reflects a structure that violates the octet rule. Thus, we cannot imagine connected molecules like Ne₂, NeF₂, F₄, OF₄, NF₅ and CF₆, and instead we may write only disconnected associations like Ne + Ne, Ne + F₂, F₂ + F₂, OF₂ + F₂, NF₃ + F₂ and CF₄ + F₂ each member of which obeys the octet rule. We may try to reinterpret such graph-theoretical observations in terms of molecular orbitals (saying that antibonding molecular orbitals are occupied in such molecules), but the phenomenon and its topological interpretation are evident. For heavier atoms (from the third and higher rows) some of the corresponding 'forbidden' structures (violating the octet rule) are realized (PF₅, SF₆, IF₇ etc.). Nevertheless, the question as to the nature of their bonds (two-centered or multicentered) is still open, and the problem is frequently revisited.⁸⁰

5.6 Molecular Disconnectedness as a Hyperperiodic Function in the Plane of Isosteric Ensembles

As discussed in Section 4.3, 'alchemical' shifts of protons do not change the general skeletal structures of molecules, particularly in Grimm series such as F₂, H₂O₂, N₂H₄ and C₂H₆. How can this Grimm rule be applied to a prototype that is a disconnected molecular pseudograph? The magic rule will be: *disconnectedness is conserved in Grimm series.*⁵⁰

Let us take an example. The molecule Ne₂ is disconnected. Consider the Grimm series associated with this molecule: Ne + HF, HF + HF, HF + H₂O and NH₃ + HF, or NH₄⁺ + F⁻, NH₃ + NH₃ and CH₄ + CH₄. Of course, the pseudographs of these molecules are disconnected, otherwise the octet rule is violated (as in, say, F - NH₄

with penta-coordinated nitrogen). The bonds of such associations of molecules are either ionic, van der Waals, or hydrogen bonds, but not the usual covalent bonds. This series has fixed Z_v and lies on a vertical line in the Plane of Isosteric Ensembles. Such disconnected prototypes appear periodically in every row with a period length of $Z_v = 6$, as in the series discussed above with Ne_2 as a prototype ($Z_v = 16$), and then NeF_2 ($Z_v = 22$), F_4 ($Z_v = 28$), OF_4 ($Z_v = 34$), NF_5 ($Z_v = 40$) etc. As a consequence, the vertical lines with disconnected Grimm series periodically cross the Plane of Isosteric Ensembles. It is possible to move from any point on the plane to one of these lines (without changing the number of heavy atoms) in either of two ways: either by the successive addition of electrons in isoatomic series (e.g. N_2 , O_2 , F_2 , $\text{Ne} + \text{Ne}$) or by successive hydrogenation steps (e.g. N_2 , N_2H_2 , N_2H_4 , $\text{NH}_3 + \text{NH}_3$). Clearly, the loss of connectedness in such a series has nothing in common with the relation between N and Z_v . Instead, only the *number of heavy atoms* is responsible for such periodic disconnectedness.

Concluding the discussion of the model for a global classification based on the Plane of Isosteric Ensembles, we should stress that this oversimplified projection serves as a crude pattern for a natural *and* periodic system of molecules. It is *natural* (according to the criteria of Section 3.1) since the disposition of molecules in such a system reflects archetypal chemical and topological features. It is *periodic* (according to Dias' criteria of Section 3.2 and also to common sense). First, it is periodic in that we may consider *many* Planes of Isosteric Ensembles differing in the number of molecular inner shells. Second, it is periodic with respect to the regular appearance of disconnectedness. This last phenomenon would be better termed hyperperiodicity. Its origin is no longer connected with the atomic periodicity and should be discussed more carefully.

6. The Hyperperiodicity Pattern: Classification of Isovalent Ensembles

Hyperperiodicity – the loss of connectedness of all members within some Grimm families – means that the isoelectronic principle does not exhaust all the possibilities of arranging molecules in equal sets. Another possibility, just discussed, is the arrangement of molecules into isovalent Grimm series. Such series have a fixed number of heavy atoms N_A but a variable number of protons (say, for the series from Ne to methane, $N_A = 1$, and for the series from CO_2 to allene, $N_A = 3$). As was mentioned earlier, similarity in skeletal structures is typical for Grimm series. It seems clear that we could construct the plane (Z_v, N_A) and investigate it in a manner analogous to our study of the Plane of Isosteric Ensembles.

A point on the (Z_v, N_A) plane represents molecules with a given number of valence electrons and with a given number of heavy atoms. Let us replace the points with cells; inside a cell the molecules are considered indistinguishable. It is reasonable to represent the families inside each of the cells symbolically by pairs of molecules, where the first one has no hydrogen atoms, and the second one has a large (or maximal) number of hydrogen atoms. The pairs ($\text{F}_2\text{-C}_2\text{H}_6$), ($\text{FNO-C}_3\text{H}_6$), ($\text{FNCO-C}_4\text{H}_6$) clearly illustrate such isovalent cells. Of course, there may be polymorphism (the three i's), and therefore the pairs ($\text{NF}_3\text{-isobutane}$) and

(F₂O₂-butane) represent the same cell with $Z_v = 26$ and $N_A = 4$, as also does the pair (SOF₂-H₂CS(CH₃)₂), where the last molecule is the dipolar sulfur ylide.

Many chemists (especially Grimm, Mulliken, and Walsh) long ago used series with fixed N_A and variable Z_v (for instance, series like H_nXY or H_nAB₂) in order to follow structural trends as a function of variable numbers of electrons and protons.^{69,70,81} Let us call such series with constant numbers of heavy atoms *hyper-rows*, considering them as finite sequences of cells ordered with increasing number of Z_v . The first hyper-row originates from the atoms (Li to Ne) and its cells include the elements with corresponding hydrides like O with BH₃ or F with CH₃. The second hyper-row starts with Li₂ and finishes with (Ne₂-C₂H₈). How do such hyper-rows with different N_A relate to one another and in what respect? Can we arrange them in some sort of a table?

Of course, every hyper-row always has a unique cell with an alkane molecule. Those cells of the first four hyper-rows are (Ne-CH₄), (F₂-C₂H₆), (F₂O-C₃H₈) and (NF₃-C₄H₁₀). Let us shift the hyper-rows in respect to one another until the cells with alkanes (and of course with their prototypes Ne, F₂, F₂O, NF₃ etc.) are arranged into a vertical column. The resulting total set of columns (which will be called the *hyper-columns*) and hyper-rows form a table. As we illustrate below, this can be considered as showing the pattern of *molecular hyperperiodicity*.⁵⁰ Such a 'hyperperiodic table' is shown in Figure 21. Only selected molecules without hydrogen atoms (one in each cell) and only cells with even Z_v are shown in this table.

The first feature of the table is that it combines the advantages of the two local tables described above: one of organic and another of inorganic molecules (see Section 4.1.1). Indeed, both of those tables – Morozov's table for hydrocarbons (Figure 8) and Haas's tables of paraelements and derivatives (Figure 9) – immediately follow as two important special cases of the hyperperiodic chart. It is simply necessary to add columns with odd Z_v and to display only specific members of the cells, either hydrocarbons and their radicals or small perfluorinated inorganic groups (paraelements).

Let us try to clarify what the difference is between molecules from different hyper-columns, and, vice versa, what sort of similarity exists between molecules from the same vertical group. Consider the series of molecules of the simplest type AB_x, where A is a central atom with x ligands B (B – electronegative atoms like oxygen or halogens). A first glance at the right-hand part of Figure 21 gives an immediate conclusion: the molecules from the same hyper-column have similar shapes, while the molecules from different hyper-columns display regular differences in their shape. A familiar example of the latter is the series of fluorides BeF₂, BF₃, CF₄, PF₅ and SF₆, where each member represents a different hyper-column. Molecular shapes within this series progress in the following order: line, triangle, tetrahedron, trigonal bipyramid, octahedron.^{81,82} Here the molecular shape is a polyhedron formed by the fluorine ligands, or (alternatively) by the bonding electron pairs. We may compare the geometries along the last few members of several hyper-rows (BeF₂-CF₂-SF₂-XeF₂, BF₃-NF₃-ClF₃, CF₄-SF₄-XeF₄ etc.) and conclude that the structural changes follow the same order as that just described.

Cyclomatic Number	***	10	9	8	7	6	5	4	3	2	1	0	Not defined		
											H ⁺	H ⁻			
									Be	C	O	Ne			
						Li ₂	Be ₂	B ₂	C ₂	N ₂	O ₂	F ₂			
			Li ₂ Be	Li ₂ C	Li ₂ O	LiCN	C ₃	LiOF	BeF ₂	FNO	F ₂ O	XeF ₂			
	Li ₄				Li ₂ O ₂	LiN ₃	C ₂ N ₂	P ₄	FN ₃	BF ₃	NF ₃	ClF ₃			
Li ₄ Be								N ₃ CN	C ₃ O ₂	N ₂ O ₃	NO ₃ F	CF ₄	SF ₄	XeF ₄	
								***				CF ₃ OF	PF ₅	IF ₅	
								Examples not shown	***			CF ₃ NF ₂	CF ₃ CF ₂	SF ₆	XeF ₆
										***		CF ₃ CF ₃	CF ₃ SF ₅	CF ₃ XeF ₅	IF ₇
Euler Characteristic	***	-18	-16	-14	-12	-10	-8	-6	-4	-2	0	2	4	6	8

Figure 21 The hyperperiodic table of isovalent ensembles of molecules (E.V. Babaev, 1988). One representative member is shown for every cell. The hyper-rows consist of molecules with the same number of heavy atoms. The hyper-columns (shown only for even Z_v) reflect similar skeletal shapes and topology, see text. (Reproduced with minor revision from ref. 50.)

(In these cases the polyhedron is formed by bonding and non-bonding lone pairs.⁸²)

The shape similarity along any hyper-column, in turn, is manifested by the series F₂O–NF₃–CF₄ (tetrahedron), XeF₂–ClF₃–SF₄–PF₅ (trigonal bipyramid) and XeF₄–IF₅–SF₆ (octahedron). There are additional sets of isosteres – AlF₃–SiOF₂–PO₂F–SO₃ (triangle), SiF₄–POF₃–SO₂F₂–ClO₃F (tetrahedron) etc. – that provide more support for the same thesis. The dependence of molecular shapes on the electron count was recognized long ago. It was explained in different ways, either in terms of the local environment of atom A (as in the hybridization model or in the Gillespie-Nyholm VSEPR-rules)⁸² or in terms of Walsh correlation diagrams (treating the geometry as a function of energy and the occupancy in the orbitals of the entire molecule).^{70,81}

By definition, cells have been arranged into hyper-columns according to the homology principle (Section 5.5.3). Homologous hydrocarbons C_nH_{2n+2} may differ by any number of CH₂ groups, and the CH₂ group bears six valence electrons. By extension, members of the same hyper-column may differ by any fragment with six valence electrons (more strictly speaking, the difference is six times the number of heavy atoms in the fragment, N_{AF}). The simplest such fragments are O and F⁺, and it is easy to see that just these ligands are responsible for the conservation of shapes

in the AB_x -type molecules (such as the triangular series $CF_2-CF_3^+-BF_3$ or the tetrahedral family $NF_3-NF_4^+-NF_3O$). These fragments, therefore, serve as the heavy-atom analogs of the proton (see Section 4.3), and their removals or additions (and even rearrangements) only slightly change the local environment of the central atoms A in molecules. More such ligands may be constructed by applying the element displacement principle⁵⁷ to the groups F^+ and O (see Figure 9 and Section 4.1.1).

The question arises, however, what sort of similarity appears between members of hyper-columns with larger numbers of atoms that are difficult (or impossible) to present as AB_x molecules? The question comes into focus by considering other examples of fragments with $6N_{AF}$ valence electrons ($-S-$, $-CH_2-$, $-CH_2O-$, $-CH(OH)-$, $-CF_2-$, $-(HO)PO_2-$, $-SO_3-$, and $-Si(OH)_2O-$), typical homological fragments which are extremely widespread in many natural (and artificial) oligomers and polymers (cf. sugars, aluminosilicates, oligomers of polysulfides, crown-ethers, polysulfuric and polyphosphoric acids etc.). Hence, the members of the same hyper-column are homological in a very general sense. Then, what is the difference between such global homological families?

Remember that the hydrocarbons are vertically arranged in homological series. A horizontal shift to the left from the alkanes leads to the hyper-column with alkenes and cycloalkanes. More shifts to the left correspond to less saturated hydrocarbons. Hence, an alternative meaning of the hyper-column number is the saturation degree (number of multiple bonds and cycles). We are no longer limited by hydrocarbons, and should remember possible inorganic cycles (e.g. S_8) or polycycles (P_4 or adamantane-like oxides E_4O_6 and E_4O_{10} , where E stands for atoms of the 5th group of the periodic table), and attribute to them an analogous 'degree of saturation'. As we proved in discussing the Plane of Isosteric Ensembles, the number of cycles (independent of their size) is an important topological feature of a molecule. How then may this topological feature be related to the trends of molecular shapes in the AB_x series?

The simplest answer is to consider geometrical similarity (for AB_x shapes) as a particular case of a more global topological similarity (homeomorphism) between the structures. Hence, we should somehow draw loops in the skeletal structures, obtain pseudographs, and consider the hyper-columns to be examples of isocyclic or homeomorphic structures. This works, if a loop is attributed to a two-electron *vacancy* in a molecule; say, to an empty p-orbital of a Lewis acid. (Thus, pseudographs of BH_3 , BeH_2 and LiH should consist of 1, 2, and 3 loops, respectively.) Then, the total number of such vacancies, double bonds, and cycles is a skeletal cyclomatic number with the clear meaning of a 'generalized electron deficiency' (considered with respect to the reference series, alkanes). This beautiful mathematical analogy has a physical background: the 'emptiness' in the middle of (a large) cycle or in an atom with a vacancy (a degenerated cycle) corresponds to a specific deficiency in electronic density.⁸³ This analogy may be widened to include the double bond (presented as a 'banana-like' bond) as the cycle of size 2.

We may conclude that the hyper-columns contain homeomorphic skeletal

structures and therefore that they can be numbered according to the cyclomatic number of the appropriate pseudographs (as shown by the numbers at the top of the Figure 21) or according to the Euler characteristics of imaginary 2D-surfaces (obtained by skeleton-inflating, cf. Section 4.3.2), see Figure 22. The Euler characteristic χ is a topological invariant that can be easily calculated for topological objects.⁷⁵ A familiar example is the famous Euler theorem $V - E + F = 2$ for a polyhedron (where V , E , and F are the number of vertices, edges and faces and $\chi = 2$ is the Euler characteristic for the sphere to which the polyhedron is homeomorphic.) The heuristic role of the Euler characteristic in chemical topology is well known.⁸⁴

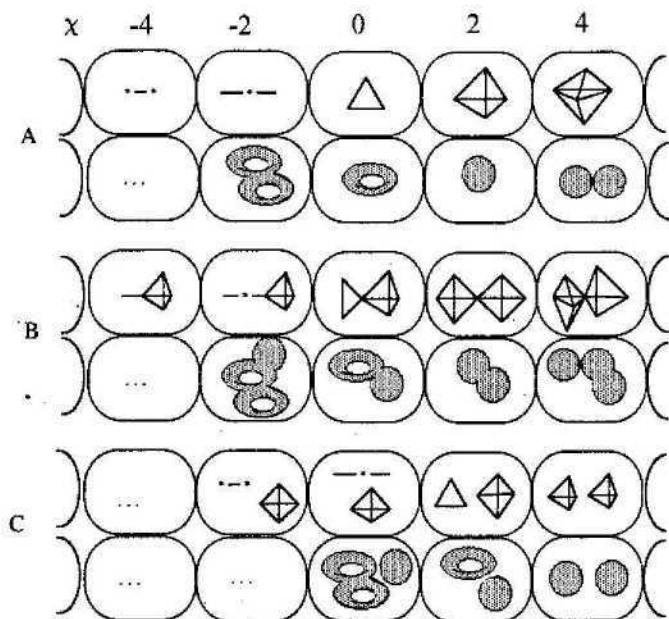


Figure 22 Geometrical and topological trends along the hyper-columns.⁵⁰ (A) Topological features (handles and χ) are changed parallel to the hybridization; (B) Insertion of tetrahedral sp^3 -fragments (with $Z_v = 6N_{AF}$) conserve χ ; (C) Total χ of a disconnected set is the arithmetic sum of χ of the connected prototypes.

For connected two-dimensional surfaces with C handles, $\chi = 2 - 2C$. A decrease of χ in going from right to left in Figures 21 and 22 is therefore paralleled by an increase of electron deficiency (due to the appearance of new 'handles' from cycles, multiple bonds, or electron vacancies). For hypervalent structures χ may also be defined⁸⁵ if one assumes such hyperconnected objects to be two-dimensional surfaces with a jointly shared point, as in Figure 22. With this in mind, a rather elegant principle – the conservation of χ – may be used to define the necessary two-dimensional surfaces for both electron-precise and electron-rich structures.^{76,85}

Finally, hyperperiodicity along a hyper-column can be treated in the following manner: insertion of specific fragments with $Z_v = 6N_{AF}$ either conserves the local environment of the atoms (i.e. molecular shape) if the inserted fragments are small, or causes structural changes which conserve the generalized electron deficiency and the key topological features of the initial structures if the fragments are large.

7. Special Types of Charts: Diatomic Molecules

Peculiarities of diatomics. The problem of molecular periodicity in series of diatomics has attracted a great deal of attention from both chemists and physicists, especially spectroscopists and quantum chemists. Most diatomics (e.g. NaCl or CaO) are obtained in the vapor phase as short-lived species, and only a few of them (e.g. diatomic halogens, O₂, N₂, CO and NO) are stable 'chemical' molecules. For this reason, classifications which include *all* diatomics have been called 'physical' systems.⁵² Actually, many scientists who studied the trends of diatomics intensively never looked at their results with respect to molecular periodicity. Sometimes, however, the regularities discovered in diatomics caused the construction of various charts called 'Periodic Tables of Diatomic Molecules'. Curiously, this term has been most frequently used by Russian chemists (since Mendeleev's time); among the independent contributors in this area are Syrkin (1960s),^{86a} Schukaryov (1970s),^{87a} Shigorin (1970s),^{86b} Kaslin (1980s),^{86c} Monyakin (1980s),^{86d} and Zhuvikin (1980-90s, in collaboration with one of us, see Section 8). A review of the early ideas, problems, and achievements in this important field is given in ref. 43.

Although diatomics are the simplest case of polyatomic molecules, there is no simplicity in their periodic classification. The existence of periodicity in many properties of diatomics was observed long ago, and many graphs with different properties plotted against different variable parameters can be found in books.^{43,87} One of the first periodic tables of diatomics was formulated by Clark in the 1930s on the basis of the periodic behavior of spectroscopic constants.^{86c} He drew a series of tables for diatomic molecules, arranging them in a simplified version of the periodic chart. Clark also devoted a great deal of effort to showing the similarity of data for isovalent molecules.

There are a few problems associated with a Periodic Table of Diatomics, but the problems can be solved. The first is that the electronic structures of diatomic molecules do not follow the same pattern as the structures of atoms. In atomic periodicity, the electron capacities of the periods and other general trends for atoms with atomic numbers up to 18 are satisfactorily explained by the simple assumption that the electronic structures are equivalent to that of a slightly perturbed hydrogen atom (where the sequence of atomic orbitals is 1s, 2s, 2p, 3s, and 3p). However, there is no such unique pattern for similarly light diatomics; for example, the orbital sequence of B₂ is different from that of F₂ (in contrast to the situation for the atoms B and F). Crudely speaking, we can neither predict an *a priori* sequence of levels nor the exact 'lengths of periods' for diatomics just as it becomes impossible to continue the simple pattern, mentioned above, for atoms beyond argon. Nevertheless, a simplified picture (occupancy of bonding and antibonding molecular orbitals by

valence electrons) qualitatively explains trends in bond lengths and other properties of diatomics and is described in most introductory courses on molecular orbital theory; furthermore, a periodic table can in principle be constructed. Regularities and irregularities in the electronic structures and terms for diatomics (consisting of atoms from the first three rows), observed and calculated by quantum-chemical methods, have been very recently reviewed by Boldyrev and co-workers, who indeed present a periodic table.⁸⁸

Comparative prediction of properties. The second problem associated with Periodic Tables of Diatomics is whether the desired properties of unknown molecules can be interpolated or extrapolated from the properties of known molecules? More specifically, which independent variables should be used in the interpolations or extrapolations? This topic has been under extensive investigation by one of us and the entire Southern College group.^{43,89} We mentioned earlier that each atom has two invariants – c (its column number) and r (its row number) – which are responsible for its similarity with, or dissimilarity to, other atoms. Consequently, any diatomic is exactly codified by four numbers (c_1, r_1, c_2, r_2) that indicate the rows and the columns of the two atoms in the molecule. In order to cover all possible atoms (including d- and f-families) the long-form periodic table with 32 columns may be used. (In such a case the value c varies from 1 to 32 and the value of r varies from 1 to 7.) Careful analysis of more than 20 properties of diatomic molecules against various combinations of these four variables (c_1, r_1, c_2, r_2) demonstrates that monotonic functions appear most often if the product $r_1 r_2$ is used for comparison.^{43,89c} (In some cases, better results can be achieved by the use of $r_1 + r_2$.)

The least-squares method permits one to make useful predictions about the properties of diatomics. One prediction was that the published room temperature entropy of gaseous MgI, 65.042 J/K^{90a} was in error. Indeed, the next edition of the data tables gave 60.3579 J/K as the entropy.^{90b} Another is that the ionization potential of the molecule CCl should be less than the published value of 12.9 eV, perhaps 10.0 eV or even lower. These isolated predictions are accompanied by hundreds of predictions for internuclear separations.⁴³

The last but not the least problem about the periodicity of diatomics is how to express it in graphical form. One simple and elegant example of a Periodic Table of Diatomics has been proposed by F.-A. Kong from China.⁹¹ The molecules on his chart are arranged in columns and rows, so that the column number is the number of valence electrons (Z_v) and the row number is the sum of the period numbers of the atoms. Thus, the alkali halide molecules NaCl, LiF, LiCl and CsI are found in column 8 and rows 6, 4, 5 and 11, respectively. Evidently, polymorphism (of different types) immediately arises in such a classification: first in respect to isovalency (say, of isosteric LiF and BeO), second in the possible degeneracy in the sum of the period numbers (say, $3 + 3 = 4 + 2$ as in the case of NaCl and KF) and third in the possibility of alternative arrangement of two different cores between two atoms from different groups. The last case is illustrated by the pair BeS and MgO,

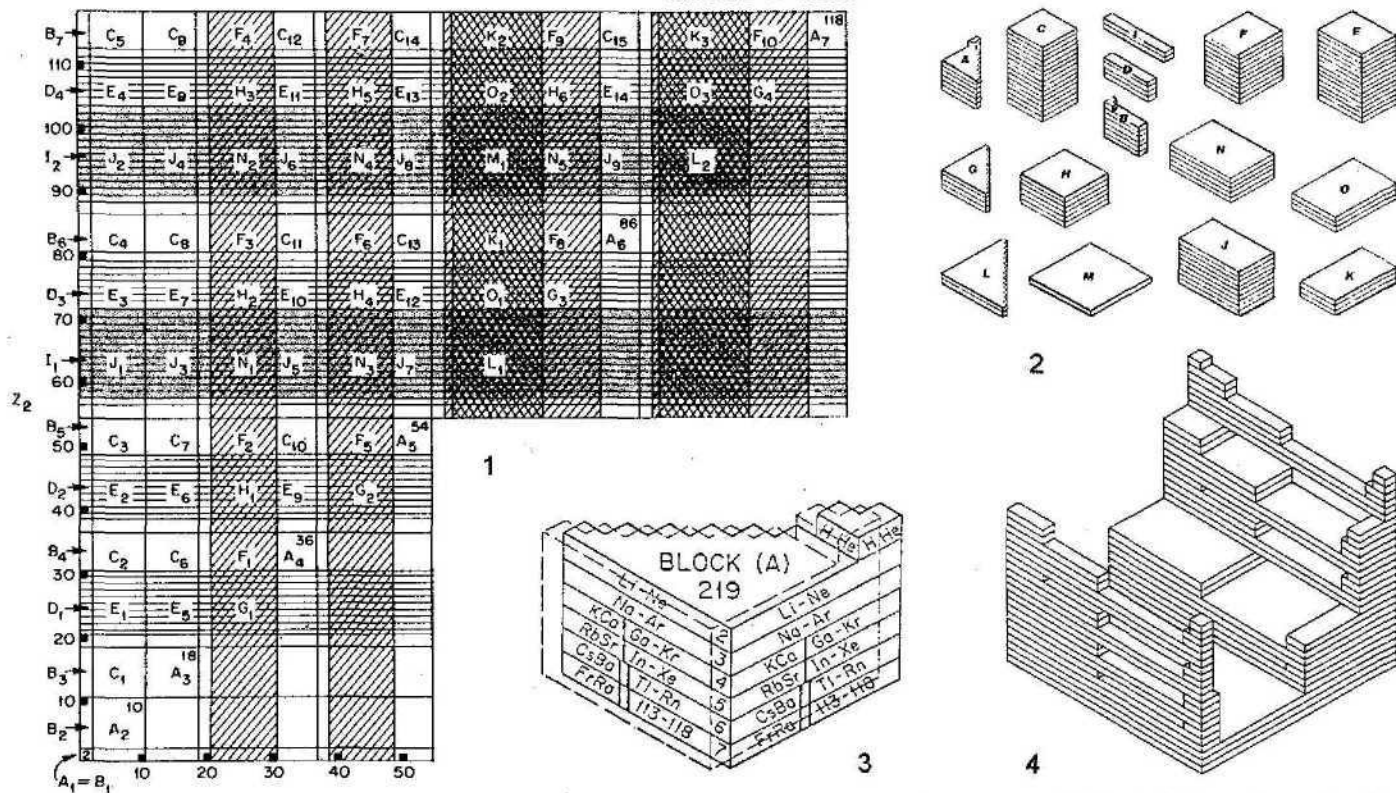
which have $(c_1, c_2) = (2, 6)$ and (r_1, r_2) either $(2, 3)$ or $(3, 2)$. Having obtained more than one molecule at the same address, Kong listed them; the list requires three pages and introduces a new descriptor, whether the difference of the atomic valence numbers is even or odd. In spite of the simplicity and polymorphism of his table, Kong predicted that the former measurement of the equilibrium separation of Ga and O atoms in the molecule GaO (reported as 0.182 nanometers) is wrong, and that it should be close to 0.172 nanometers.

Graphical Variants of Periodic Tables of Diatomics. How can the problem of polymorphism in a Periodic Table of Diatomics be avoided, and how does the entire periodic table of diatomics (without polymorphism) look? The experience of the Southern College group provides a few possible answers to these questions. The simplest chart (actually, Table) of diatomics arises if one simply considers a Cartesian lattice with coordinates Z_1 and Z_2 , i.e. the numbers of electrons for each atom (Figure 23-1). The maximum Z_{\max} is considered to be that of the hypothetical element 118; the entire number of diatomics therefore is $1/2 Z_{\max} (Z_{\max} + 1) = 7021$. Special lines (horizontal and vertical) across the chart show the boundaries between s-, p-, d-, and f-elements. With the goal to visualize the similarities and dissimilarities between diatomics, similarly shaped areas between the boundaries are similarly hatched and labeled as shown on Figure 23-1.

In order to express the relationship between similar and dissimilar domains of the above lattice more clearly, the cut-and-stack principle could be applied^{43,89b}: the similar areas can be cut and stacked upon each other. The areas with homonuclear molecules can be shorn of redundant heteronuclear molecules so that they are triangular instead of square. Finally, the interrupted pieces can be spliced together, and the entire periodic system of diatomic molecules will consist of 15 blocks (Figure 23-2). An example of one block (A) is presented in Figure 23-3. This Periodic Table of Diatomics may be considered as a disconnected set. As one alternative way of stacking the domains in Figure 23-1, we may imagine the connected three-dimensional object in Figure 23-4. The top seven layers of this arrangement pertain to molecules with H and He atoms, while the three bottom layers consist of molecules from heavy atoms with Z from 87 to 118.⁴³ The periodic system shown in Figure 23-2 corresponds very well with data for many properties of diatomic molecules, but that shown in Figure 23-4 does not.

It is possible to imagine a repetition of this entire process for molecules with any one of the possible degrees of ionization. Figure 23-4 shows the spatial relationships of block A of the Periodic Table of Unipositive Diatomic Ions to block A of the Periodic Table of Diatomics. The rationale for the lateral displacement is based (see refs. 43, 89d) on the fact that the similarities of the electron structures of molecular pairs such as N_2^{++} and C_2 would allow the twice-ionized species to be located at the same addresses as those of the neutral species. The Southern College group has devoted a great deal of effort to the relationships of ionized diatomics to neutral diatomics.^{43,89d,89e}

We can suppose that the existence of four invariants for every diatomic $(c_1, r_1,$



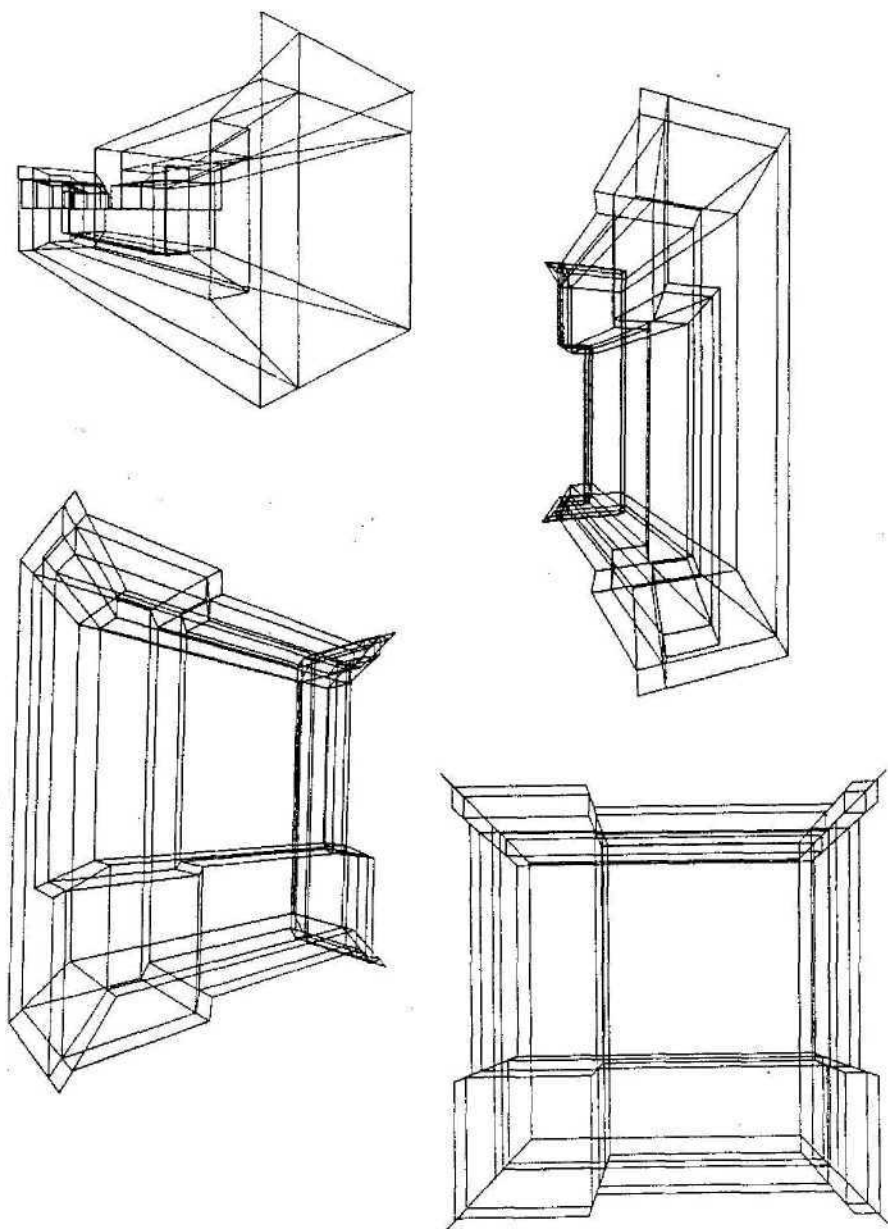


Figure 24 Different projections on a computer screen of a four-dimensional object, obtained by self-multiplication of the periodic table of atoms, illustrate a possible structure of the periodic chart of diatomic molecules. (Taken with permission from ref. 43.)

c_2, r_2) corresponds to a sort of four-dimensional object. It is easy to see why this should be. The process of combining all possible atoms with each other, two at a time, results in the formation of all possible diatomic molecules. This process is represented symbolically by combining the periodic chart of the atoms, which is two-dimensional, with itself, thus producing a four-dimensional periodic system of all possible diatomic molecules.^{43,89d,92a}

If the periodic chart of the elements were a perfect square, then the molecular system would be a hypercube. The periodic chart actually consists of one or more rectangular shapes, and so the molecular system will consist of one or many rectangular hyper-parallelepipeds. If one takes the medium form of the periodic table (without rare-earth elements) and performs its self-multiplication, the resulting object will be the four-dimensional system of diatomics containing no rare-earth elements. This architecture of the object^{43,92b} has been constructed with the help of a computer program by the Southern College group. The object can be formally rotated, and a few of the projections obtained on the computer screen are presented in Figure 24.

8. Conclusion

The problem of the global periodic system of molecules remains, for, as we have shown, there may be more questions than answers in this field. Among our promising recent achievements are novel applications of compact^{92a,93-95} and non-compact^{95,96} groups to formulate Periodic Tables of Diatomic and Triatomic molecules (where the irreducible presentations are treated as molecular multiplets), the analysis of organic reactivity in respect to the diagonal similarity in the hyperperiodic table (the 'super-consonant theorem')⁹⁷ and attempts of periodic classifications of special classes of chemical reactions.⁹⁸

The paradigm of global molecular classification may be helpful in teaching, understanding and unifying chemistry. In some respects such a 'pure chemical' paradigm is complementary to the quantum-chemical approach. Indeed, a quantum chemist requires no knowledge of molecular kinship to calculate a property (although the programmer may well need it). However, sooner or later he or she calculates many properties for many molecules and hence needs somehow to arrange the numerous data.

We may ask: to which branch of science should we attribute the art and logic of natural and periodic molecular classifications? Molecules are objects of chemistry and physics, and their classification (as we have seen) requires rather delicate mathematical models. In order to define the appropriate place of such an activity, we may arrange the so-called exact sciences in some sort of a 'periodic table':

	Physics	Chemistry	Mathematics
Physical	Pure & Applied Physics	Physical Chemistry	(Physical Mathematics)
Chemical	Chemical Physics	Pure & Applied Chemistry	(Chemical Mathematics)
Mathematical	Mathematical Physics	Mathematical Chemistry	Pure & Applied Mathematics

The vertical 'groups' are pure sciences, while the rows are their applications to other sciences. It is easy to see familiar sciences such as chemical physics, and physical chemistry, and the branches of applied mathematics. (These terms may be observed, say, as the names of scientific journals, that 'periodically' appear in libraries.) We can 'predict' two new (still little-known) sciences in the upper-right corner of the table, namely physical and especially chemical mathematics. We may remember that there are relatively new disciplines called chemical topology and chemical graph theory⁶³ (*not with reversed word order*), and that these fields are most closely related to the problems discussed in this chapter. It seems that global molecular classifications may be related specifically to chemical mathematics. Let us explain why.

Mathematicians often develop ideal objects and forms without any idea how to apply them to real physical and chemical objects of the universe. Vice versa, chemists often propose pragmatic, empirical generalizations about real objects (e.g. homology, isovalency, isomerism, aromaticity, degree of saturation, the octet rule, and the repulsion of electron pairs) without any idea how these concepts relate to one another in a mathematical sense. As we have seen, the *interrelation* between such archetypal chemical concepts is clearly displayed and clarified in global molecular classifications. Surprisingly, such interrelations appear to have the same nature and the same beauty that exists in rather abstract mathematical objects (homeomorphism of surfaces, connectedness of graphs, properties of partitions etc.). We can say that we are applying chemistry to mathematics and finding ideal mathematical forms *inside* chemistry, rather than bringing a mathematical model *to* chemistry.

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