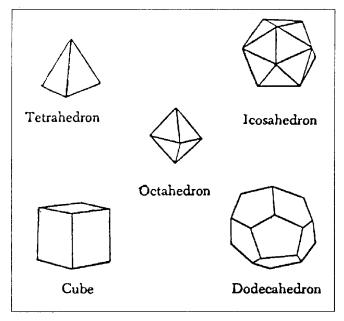
PERSPECTIVES LECTURE

Precursors and Cocursors of the Mendeleev Table: The Pythagorean Spirit in Element Classification

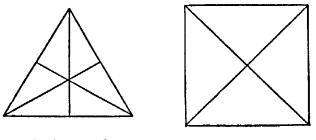
O. Theodor Benfey, Chemical Heritage Foundation

The ancient Pythagorean faith in simple numerical patterns as guides to the structure of the natural world constantly reappears in science. The Pythagoreans worshipped numbers and by numbers they meant whole numbers - integers. Since two points can define a line, three a plane and four a threedimensional body, they believed all reality could be subsumed by whole numbers and geometry. The Cubist movement in art hints at the Pythagorean vision. That vision, that religious movement, was shattered by the discovery of irrationals, unreasonable quantities that were incapable of being expressed as ratios or other combinations of whole numbers. The square root of 2, the reciprocal of 7 and the ratio of the circumference to the diameter of a circle are examples.

The simplest Pythagorean principle is the search for identity. The identity of the velocity of light and of electromagnetic waves united optics and electromagnetic theory. The next simplest is the identity in the number of members of two sets. The four elements of Empedocles - earth, air, fire and water found a counterpart in the discovery of four regular solids - the tetrahedron, octahedron, icosahedron and cube. The belief grew that there must be a connection between them. When the fifth (and last) regular solid, the dodecahedron, was discovered, a fifth element was postulated that corresponded to it. It became the quintessence, the fifth essence, the ether of antiquity. Since terrestrial events were sufficiently described by the



The five regular polyhedra or Platonic solids.



Plato's Triangle

Plato's Square

Plato's building blocks for the equilateral triangle and the square.

four elements, the fifth element was relegated to the heavens. It was a logical assignment since the behavior of celestial bodies differed from that of objects on earth. Since the natural motions of earth, air, fire and water when displaced from their normal abode were rectilinear, returning to their "proper" place, celestial motions, which were circular rather than linear, must be due to a different kind of stuff, of which the heavens were made. Behavior was seen as integral to an object, not something imposed upon it.

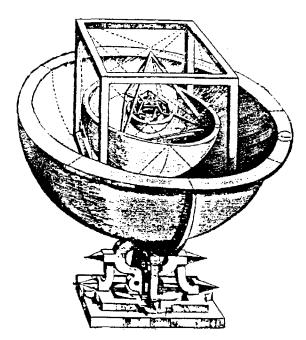
Plato in the *Timaeus* spells out the identification of regular solids with the elements of antiquity. The atoms of fire are the sharpest, hence tetrahedra; the next sharpest are octahedra which are assigned to air since it too can slip through very small interstices. Earth is the most stable, hence corresponds to the cube. The dodecahedron is the closest to the sphere, thus fittingly belonging to the heavens, leaving the icosahedron as the form of the atom of water.

We need to recognize the genius of Plato's view. First it accounted for transmutation. Since tetrahedra, octahedra and icosahedra were all made from equilateral triangles, they could be taken apart into their constituent triangles and reassembled into new forms. These transformations were quantitative. The eight faces of two tetrahedra can be taken apart and reassembled into those of one octahedron. One water particle (20sided icosahedron) can be changed into two air particles and one fire particle. We have here a universe made up of a small number of particles which, by rearrangement, make up the phenomena we observe. It is the form of the descriptive pattern we now use in describing nuclear transformations. The more commonly accepted precursor of modern atomic theory, the atomism of Democritus and Leucippus, had neither of these two key characteristics. Those thinkers postulated an unlimited number of different atoms and had no quantitative predictive theory for explaining change.

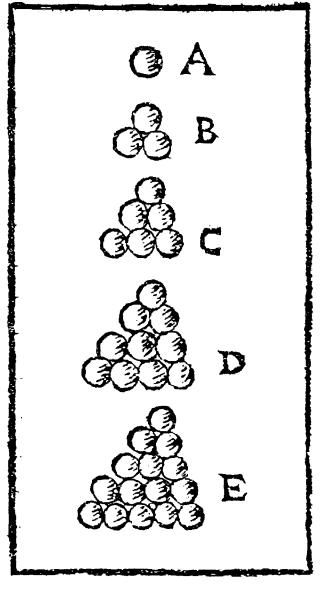
The second of Plato's contributions to element theory is more speculative. Karl Popper has suggested that Plato's choice of atoms was designed to overcome the Pythagorean scandal. Plato's atoms were actually the half-equilateral triangle (for tetrahedron, octahedron and icosahedron) and the half-square for the cube. These two triangles have sides in the ratios of 1, 2, $\sqrt{3}$ and 1, 1, $\sqrt{2}$ respectively, thus incorporating two of the Pythagorean irrationals into the fundamental building blocks of nature. Popper further suggests that the hope existed that all irrationals could be derived from $\sqrt{2}$ and $\sqrt{3}$. Their sum, for instance, to four significant figures is 3.146, a figure within the limits of accuracy of the calculation of π of that era (1). Thus irrationals, though not exactly banned from the universe, were at least tamed. They were incorporated into the building blocks of nature.

The dream of finding a numerical pattern to the phenomena of nature lay in abeyance for centuries. Although the *Timaeus* was the only dialogue of Plato translated into Latin during the ancient period, the sections of the *Timaeus* dealing with the regular solids were not included in the early Latin versions (2). The prevailing description of terrestrial nature throughout the medieval period was the qualitative Aristotelian world-view. Mathematical perfection could only be found in the heavens. Only as we enter the period of the Renaissance do we again find significant attempts to correlate what we would call chemical events with numbers.

The most famous Pythagorean or Neoplatonist of the Renaissance was no doubt Johannes Kepler (1571-1630). His most celebrated attempt to apply the Pythagorean vision was his rationalization of the sizes of the planetary orbits by inscribing and circumscribing the orbits with the Platonic solids. But Kepler did not confine his interest to the heavens. In his work, *The Six-Cornered Snowflake*, he proposed an essentially modern explanation for the snowflake's shape in terms of the packing of spheres. L. L. Whyte, in the preface to the new edition of Kepler's booklet, describes it as "the first recorded step to-



Planetary orbits and the regular solids. (from Kepler's *Mysterium cosmographicum* of 1596).



Kepler's use of sphere packing to explain crystal forms.

wards a mathematical theory of the genesis of inorganic or organic forms (3)."

The iatrochemist William Davisson (1593-1669) was equally convinced that number and geometry were the key to understanding nature. One of two engraved plates in his *Les élémens de la philosophie de l'art du feu ou chimie* of 1651 shows the Platonic solids followed by 15 other geometric forms. The opposite page shows natural forms - crystals, flowers, leaves and the beehive hexagon, to illustrate the Biblical phrase written in Latin across the center of the page: "all is disposed in measure, number and weight."

The Pythagorean fascination with integers makes a permanent reentry into chemistry with John Dalton's (1766-1844) chemical atomic theory. Antoine Lavoisier's (1743-1794) emphasis on weight relations led logically to the determination of percentage compositions. But what assurance of being on the right path of theory is contained in the fact that the lower oxide of carbon contains 57.1% oxygen while carbonic acid gas contains 72.7% oxygen? Dalton's atomic theory gave a visualizable model for the Pythagorean law of multiple proportions: For two compounds of elements A and B, the weights of A combined with a fixed weight of B are in the ratio of small whole numbers. Thus, recalculating the composition data, 1 g carbon combines either with 1.33 grams of oxygen or 2.66 grams of oxygen, an integral ratio of 1 to 2.

Another Pythagorean pattern was proposed within six years of the completion of Dalton's book New System of Chemical Philosophy. In 1816, the physician William Prout (1785-1850), whose quantitative analysis of natural urea was used by Friedrich Wöhler (1800-1882) to compare it with the urea he had accidentally made synthetically, pointed to the remarkable fact that most atomic weights used at that time were close to integral multiples of the atomic weight of hydrogen. That particular Pythagorean venture has, of course, had a checkered history, being espoused by some, such as Thomas Thomson (1773-1852), as true, by others, such as Jean-Servais Stas (1813-1891), as pure illusion, while Jean-Charles Marignac (1817-1894) accepted it as an ideal law analogous to the ideal gas laws and Dmitri Mendeleev (1834-1907) hinted at a massenergy interconversion to account for the deviations. There can be little doubt that Prout's proposal acted as a most powerful stimulus to accurate atomic weight studies and encouraged others to look for additional numerical patterns in the atomic weights slowly being accumulated.

Even if Prout's simple proposal had been right, if all atoms were in fact aggregates of hydrogen atoms, such a conclusion would have done little to illuminate the richness and diversity of chemical behavior. It certainly was not the final clue, because the elements then would only differ quantitatively and progressively as their atomic masses increased. Johann Wolfgang Döbereiner (1780-1849) from 1816 to 1829 searched for numerical relations between similar elements in the same way that the Pythagoreans sought number patterns relating the lengths of strings producing harmonious chords. Döbereiner's triads not only demonstrated such arithmetic relations but thereby suggested unit building blocks converting atoms of lithium to those of sodium and hence to potassium, or calcium to strontium and then to barium. Döbereiner was influenced by the Romantic movement and Naturphilosophie which had been flourishing in Jena around 1800, a decade before Döbereiner's arrival. "His predilection" according to Alan Rocke, "was toward a Pythagorean synthesis, the mathematization of nature" (4).

The idea of unit building blocks gained support from Max Pettenkofer (1818-1901) who pointed to the analogy between an atomic weight series of similar elements and the pattern of molecular weights in organic homologous series (5). Thus $CH_4 = 16$, $C_2H_6 = 30$, $C_3H_8 = 44$, etc. The common increment

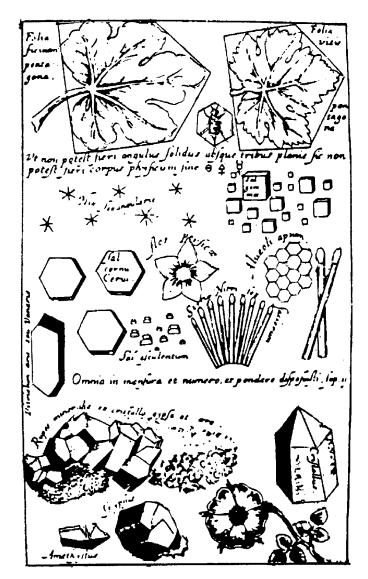


Plate from William Davisson's *Les élémens de la philosophie de l'art du feu ou chimie* showing natural forms with shapes similar to those of regular solids.

(of 14) in these weights suggested that perhaps organic radicals held the clue to the internal structure of inorganic atoms. Jean-Baptiste André Dumas (1800-1884) and Justus Liebig (1803-1873) had already proposed in 1837 that organic radicals play in organic chemistry the role played by atoms in mineral (or inorganic) chemistry (6):

In mineral chemistry the radicals are simple; in organic chemistry the radicals are compound; that is all the difference. The laws of combination and of reaction are otherwise the same in these two branches of chemistry.

What Pettenkofer was now proposing was that the radicals or

atoms of mineral chemistry were not simple - they were as compound as were organic radicals because the same mathematical patterns occurred in the unit masses of both.

Dumas developed these ideas about the composite nature of atoms independently in 1851 in a speech before the British Association for the Advancement of Science but only published them six years later (7). His parallel tabulations of organic radicals and families of elements (Table 1) show that he had freed himself from Döbereiner's preoccupation with sets of three elements, and that he was developing the families of elements as they would later be incorporated in the periodic table.

John Alexander Reina Newlands (1837-1898) broke away from searching for numerical patterns in the atomic weights of similar elements and proclaimed instead a pattern for all elements, similar or dissimilar. He did not need the actual values of atomic weights; all that was needed for his law of octaves was a rank order, the ranking of elements in order of increasing atomic weight. In some of his earlier tables Newlands left gaps for missing elements - Mendeleev certainly was not the first to do this - but by 1864 he had found an arrangement not requiring gaps and obeying his now famous law of octaves, though he did not give it this name until 1865 (8). On presenting it at a meeting of the London Chemical Society, the British chemist George Carey Foster posed the immortal question of whether a similar pattern might exist if elements are arranged alphabetically. Carey Foster clearly did not comprehend the essence of the Pythagorean discovery - that numerical order lies in the essence of things while alphabetical order is man-made and arbitrary. What Newlands discovered was an orchestration of the elements, a periodicity, a repetition combined with novelty, the essence of all musical composition. It would have delighted Pythagoras (9).

And yet something was missing. Except for the atomic weight order, why do the alkaline earths follow the alkali metals rather than the halogen family? Was there any intrinsic pattern that linked elements of *different* families, that would show an essential order to the relation among families? The year 1864, the same year as Newlands' law of octaves, saw the publication of the first edition of Julius Lothar Meyer's (1830-1895) *Die Modernen Theorien der Chemie* (10). Meyer was fascinated by Prout's hypothesis, by Döbereiner's triads and

by Pettenkofer and Dumas' analogies between chemical element families and organic homologous series. He had attended the Karlsruhe Congress in 1860 as had Mendeleev. Both had been deeply influenced by Stanislao Cannizzaro's

	No		No.		No.			No.			No.		No.			No.		N
	I		8	Cl	15	Co	& Ni	22	Br		29	Pd	- 36	I		42	Pt &	Ir (
					16			23	RЬ			Ag					Os	į
G	3	Mg	10	Ca	17	Zn		24	Sr		31	Cď	-38	Ba	& V		Hg]
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С	-5	Si	12	Ti	18 1 20	In		26	Zr		32	Sn	39	W		47	РЪ	Ì
Ν	ő	P	13	Mn	1 20	As		27	Di &	Mo	34	Sb	41	NЬ		48		
С	7	S	14	Fe	21	Se		28	Ro &	: Ru	35	Te	43	Au		40	Th	-

Newland's Table of Octaves of 1865.

$CH_3 = C_2H_5 = C_3H_7 =$	1 + (0 x 14) 1 + (1 x 14) 1 + (2 x 14) 1 + (3 x 14) 1 + (4 x 14)	0 = 8 S = 8 + 8 Se = 8 + (4 x 8) Te = 8 + (7 x 8)	= 8 = 16 = 40 = 64
		N = 14 P = 14 + 17 As = 14 + 17 + 44 $Sb = 14 + 17 + (2 \times 44)$	= 14 = 31 = 75 = 119

(1826-1910) speech and pamphlet. Meyer later wrote how, on reading the booklet, "the scales fell from my eyes and my doubts disappeared and were replaced by a feeling of quiet certainty." His *Moderne Theorien* was a direct outcome of that experience. Calculating all atomic weights according to Cannizzaro's principles, he arranged them by increasing atomic weight and in families, and calculated the increments of weight from each atom to the next similar one. So far nothing was new. But when we look at the table he published of 27 elements arranged in this way, three remarkable facts stand out:

1. He leaves a gap between silicon and tin and estimates the atomic weight of the missing element to be 28.5 + 44.55 = 73.05. Germanium's atomic weight was later found to be 72.59. Newlands had also done this in 1864.

2. He places tellurium *before* iodine in spite of the fact that its atomic weight, 128.3 is greater than that of iodine (126.8). Newlands also did this.

3. Most impressive of all, he places at the heads of the families the notations 4-werthig, 3-werthig, 2-werthig, 1-werthig, 1-werthig, 2-werthig, that is successive valences of 4, 3, 2, 1, 1, and 2. These are the valences toward hydrogen, the number of hydrogen atoms that attach themselves to an atom of the element.

The fact that water was H_2O and not HO, and that oxygen therefore was divalent, was not universally accepted until after the Karlsruhe Congress. Within organic chemistry, Avogadro's

> hypothesis (based on that other Pythagorean law-Gay-Lussac's law of combining volumes) had been widely accepted particularly by Auguste Laurent (1807 -1853) and Charles-Frédéric Gerhardt (1816-1856) in their thorough reexamina

tion and reorganization of organic theory. Alexander Williamson's (1824-1904) studies of ethers had established the water type and divalent oxygen, August Wilhelm Hofmann's (1818-1892) amine work did the same for the ammonia type and the trivalence of nitrogen. Friedrich August Kekulé (1829-1896) in 1857 rescued organic radicals from being looked at merely as good substituents in inorganic type formulas, and established methane as the parent type of all carbon compounds and hence gave carbon a valence of 4. Laurent and Gerhardt accepted and universalized Avogadro's conclusion beyond the property. The only places where sets of new elements could be located would be at the beginnings and ends of each horizontal series, or at the beginning of the whole list or beyond the heaviest element. Meyer organized 21 other elements in seven further families which can be appended to the earlier table but do not show the stepwise change in valence. They are all transition metals.

No one, it seems, suspected that from a purely numerical point of view there was in fact one other place for new elements - between the two univalent families, a family of valence zero.

ready applicability of Avogadro's hypothesis. They tended to assume that all elements, not only the common gaseous ones, were composed of diatomic molecules. With that assumption formulas of numerous inorganic compounds looked most unlike the formulas of today. Cannizzaro's reform introduced two other major criteria for atomic weight

4	val.	3 val.	2 val.	ı val.	ı val.	2 val.
	• • • •		••••		Li 7.03	(Be 9.3)
		••••			16.02	(14.7
C	12.0	N 14.4	O 16.00	F 19.0	Na 23.5	
Diff.	16.5	16.96	16.07	16.46	16.08	16.0
		P 31.0				
Diff. Ag	1 44.45	44.0	46.7	44.51	46.3	47.0
2		As 75.0	Se 78.8	Br 79.07	Rb 85.4	Sr 87.0
Diff. 89-	1 44.55	45.6	/0.5	46.8	47.6	40.0
					Cs 133.0	49.0
					35.5	
Ph. 2	44·/	2 43.7 Bi 108 0			(T1 204.0?)	Do tom t
						ba 137.1
4 va (Ministri	.i. - -	4 val.		2 val.	I Val.	
$\int \mathbf{E} \mathbf{n} \mathbf{E}$	5.1	Ni 58.7	C0 50.7	20 05.0	Cu 03.5	
(16 30						
D;# 49	j .2	156	45.0	16 0		
	2 1	45.0	47.3	40.9	44•4	
149 D		45.6 Rh 104.3	Dd rof o	Cd III o	1 ~ 107 01	
		•••			0	
		$\frac{92.8}{2}$ 46.4				
Pt 10	7.I	Ir 197.1	Us 199.0	Hg 200.2	Au 196.7	

The absence of any expectation of such a family reminds us of the centuries that it took before the zero symbol was introduced into the Hindu-Arabic numeral notation - before zero was recognized as a number.

Mendeleev'speriodic table of 1869 was characterized by his successfully arranging *all* the elements into one table and in demonstrating that

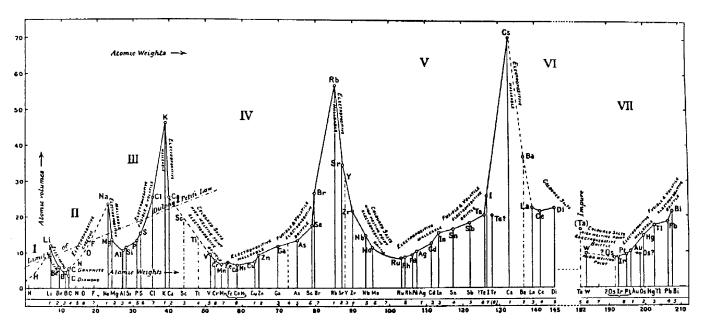
Lothar Meyer's table of 1864.

determinations, particularly useful for elements that do not readily form gaseous compounds. Besides Avogadro's hypothesis, he used as guides the law of Pierre-Louis Dulong (1785-1838) and Alexis-Thérèse Petit (1791-1820) and Eilhard Mitscherlich's (1794-1863) law of isomorphism.

Meyer's book in its first edition was in large measure a detailed exposition of the application of these three methods. With them formulas could now be confidently established, and when they were examined a new pattern emerged. The elements from carbon to magnesium change by one valence unit, decreasing first to unity and then increasing again. The same pattern recurs from silicon to calcium, from arsenic to strontium, from tin to barium. No element is expected to be found between any pair of successive elements, for valence can only change by integral steps. It was a true Pythagorean periodicity holds throughout. His 1871 table clearly indicates that valence periodicity, by integer-unit steps, applies to all elements.

It appears that Mendeleev was extremely skeptical of any Pythagorean or Proutian implications of his work, considering them mere utopias. Yet he did much to suggest their significance (11).

There seems to be no question now that Meyer and Mendeleev independently discovered the periodic law. For a number of years a somewhat bitter debate raged between Mendeleev and Meyer regarding the original contributions of each to the chemical literature. Meyer's paper was submitted in December 1869 and published in March 1870 (12) and refers to the brief German notice of Mendeleev's longer paper in Russian (13). Meyer, in that paper, published the atomic volume



Lothar Meyer's atomic volume versus atomic weight curve as redrawn by Thomas Bailey for the Philosophical Magazine in 1882.

curve for which he is most generally remembered. However, we need to recognize that Mendeleev as well as Meyer in their classic papers discuss both atomic volume and other properties which vary periodically as atomic weight rises.

Meyer begins his paper with the assertion that it is most improbable that the chemical elements are absolutely undecomposable and mentions Prout, Pettenkofer and Dumas as precursors of this idea.

In 1893, two years before Meyer's death, his successor, Adolf Remelé, at the School of Forestry in Neustadt-Eberswalde, showed him a handwritten draft of a periodic table which Meyer had given to him in July 1868 and which was intended for a new edi-

er's independ-

ent arrival at a

table contain-

ing almost all known elements, arranged by increasing atomic weights and in periods, with the A and B subgroups separated, and with a gap left between silicon and tin suggesting the future discovery of germanium. Meyer's table places lead correctly below tin (column 8) while Mendeleev had put it with calcium, strontium and barium. On the other hand, hydrogen, boron and indium are not on the table, presumably because Meyer did not know where to locate them. The 1868 table was published posthumously by Karl Seubert, Meyer's successor in Tübingen (14). Mendeleev and Meyer were recognized as independent developers of the periodic table of the elements by the Royal Society of London when they were

tion of the Moderne	I	2	3	4	5	6	7	8
Theorien. Meyer had to- tally forgotten the existence	Cr=52.6	Mn=55.1 49.2 Ru=104.3 92.8=2.46,4 Pt=197.1	A1=27.3 23.7=14.8 Fc=56.0 48.9 Rh=103.4 92.8=2.46.4 1r=197.1	A1-=27.3 Co=58.7 47.8 Pd=106.0 93=2.465 Os=199.	Ni=58.7	Cu=63.5 44.4 Ag=107.9 89.8=2.44.4 Au=196.7	Zn=65.0 46.9 Cd==111.9 88.3=2.44.5 Hg=200.2	C == 12.000 16.5 Si == 28.5 *3 -1 == 44.5 Sn == 17.6 Sg 4 == 2.41.7 Pb == 207.0
of this draft since, after	. 9	10	п	12	13	14	15	
Mendeleev's 1869 paper, it had to be redone. It de- monstrated clearly Mey-	N = 14.4 16.96 $P = 31.0$ 44.0 $A = 75.0$ 45.6 $Sh = 120.6$ $87.4 = 2.43.7$ $Bi = 20%.0$	O = 16.00 16.07 $S = 32.07$ 46.7 $S = -78.8$ 49.5 $T = = 128.3$	F = 19.0 r6.46 C1=35.46 44.5 ltr=79.9 46.8 1 = 126.8	$\begin{array}{c} 1.1 = 7.03 \\ 16.02 \\ Nn = 23.05 \\ 16.08 \\ K = 39.13 \\ 46.3 \\ Rb = 85.4 \\ 47.6 \\ Cs = 133.0 \\ 71 = 2.35.5 \\ Tc = 204.0 \end{array}$	Be=9.3 14.7 Mg=24.0 16.0 Ca=40.0 47.6 Sr=87.6 49.5 Ba=139.1	Ti==48 42.0 Zr==50.0 47.6 Ta==137.6	Mo.=92.0 45.0 Vd=137.0 47.0 W=184.0	

both awarded the Davy medal in 1882.

The Periodic Table was not by any means the final triumph of the Pythagorean dream in element classification. Prout's hypothesis was shown to be essentially

Lothar Meyer's unpublished table of 1868. (from F. P. Venable, The Development of the Periodic Law)

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correct as far as the weights of individual nucleides were concerned. Non-integral atomic weights are mainly due to the presence of isotopic mixtures in the usual samples of elements. The ordinal number of Newlands' "rank order" of elements became identified in 1913 by Henry Gwyn-Jeffries Moseley (1887-1915) with the number of increments that the square root of the frequency of X-rays must be shifted to predict the correct X-ray frequency for a given element (15). The ordinal number became the atomic number, the integral positive charge and number of protons of an atom's nucleus and the number of electrons surrounding it. But these Pythagorean identifications once again did not account for the diversity of chemical properties. That was achieved by arranging the electrons in superbly simple Pythagorean patterns, by recognizing that similar chemical properties imply similar arrangements of electrons. We are the true inheritors of an idea 2500 years old - that the properties of the elements are the properties of numbers (16).

References and Notes

Acknowledgments: An early version of this paper was presented at the Mendeleev Symposium, December 1969, Annual Meeting of the American Association for the Advancement of Science. It was originally prepared for publication to honor the chemist and chemical educator Ronald J. Gillespie on his 65th birthday, but was considered too historical for the special issue (November 1989) of the Canadian Journal of Chemistry published in his honor.

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16. Since writing the original draft of this lecture several additional references have come to my attention. W. B. Jensen, "Classification, Symmetry and the Periodic Table," *Comp. & Maths. with Appls.*, **1986**, *12B*(*1*/2)487-510, has examined the structure and development of the periodic table in the light of a wide range of contemporary mathematical concepts. These observations have been further expanded within an historical context in his *From Triads to Aufbau: Twelve Lectures on the Nature and History of the Periodic Law*, based on lectures given at the 1991 Beckman Center Workshop on the History of Chemistry and at the 1992 Woodrow Wilson Institute at Princeton and due to be published next year. Also of great interest is the paper by E. Ströker, "Die Ordnung der Elemente: Entstehung und Bedeutung des Periodensystems," in W. Sawodny, R. Opferkuch, and A. Schunk, eds., *Chemie im Spiegel der Jahrhunderte*, Universitätsverlag, Ulm, 1992, pp. 67-79.

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BOOK NOTES

Curiosity Perfectly Satisfyed: Faraday's Travels in Europe 1813-1815, Edited by Brian Bowers and Lenore Symons, Peregrinus, London, 1991. xvi + 168 pp. Cloth (Typeset), \$33.00. Michael Faraday's 'Chemical Notes, Hints, Sugges-