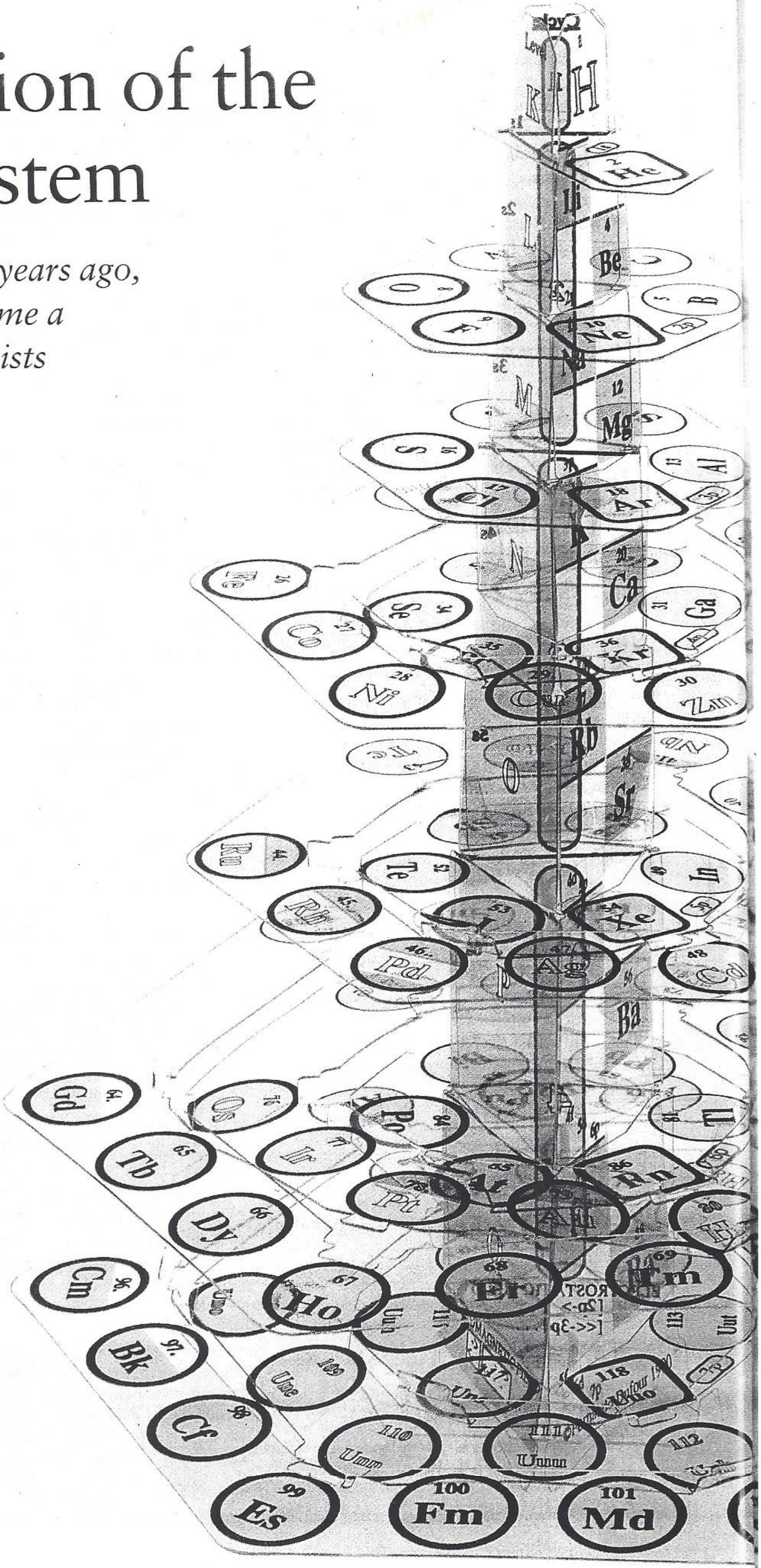
The Evolution of the Periodic System

From its origins some 200 years ago, the periodic table has become a vital tool for modern chemists

by Eric R. Scerri



The periodic table of the elements is one of the most powerful icons in science: a single document that consolidates much of our knowledge of chemistry. A version hangs on the wall of nearly every chemical laboratory and lecture hall in the world. Indeed, nothing quite like it exists in the other disciplines of science.

The story of the periodic system for classifying the elements can be traced back over 200 years. Throughout its long history, the periodic table has been disputed, altered and improved as science has progressed and as new elements have been discovered [see "Making New Elements," by Peter Armbruster and Fritz Peter Hessberger, on page 72].

But despite the dramatic changes that have taken place in science over the past century—namely, the development of the theories of relativity and quantum mechanics—there has been no revolution in the basic nature of the periodic system. In some instances, new findings initially appeared to call into question the theoretical foundations of the periodic table, but each time scientists eventually managed to incorporate the results while preserving the table's fundamental structure. Remarkably, the periodic table is thus notable both for its historical roots and for its modern relevance.

The term "periodic" reflects the fact that the elements show patterns in their chemical properties in certain regular intervals. Were it not for the simplification provided by this chart, students of chemistry would need to learn the properties of all 112 known elements. Fortunately, the periodic table allows chemists to function by mastering the properties of a handful of typical elements;

all the others fall into so-called groups or families with similar chemical properties. (In the modern periodic table, a group or family corresponds to one vertical column.)

The discovery of the periodic system for classifying the elements represents the culmination of a number of scientific developments, rather than a sudden brainstorm on the part of one individual. Yet historians typically consider one event as marking the formal birth of the modern periodic table: on February 17, 1869, a Russian professor of chemistry, Dimitri Ivanovich Mendeleev, completed the first of his numerous periodic charts. It included 63 known elements arranged according to increasing atomic weight; Mendeleev also left spaces for as yet undiscovered elements for which he predicted atomic weights.

Prior to Mendeleev's discovery, however, other scientists had been actively developing some kind of organizing system to describe the elements. In 1787, for example, French chemist Antoine Lavoisier, working with Antoine Fourcroy, Louis-Bernard Guyton de Morveau and Claude-Louis Berthollet, devised a list of the 33 elements known at the time. Yet such lists are simply one-dimensional representations. The power of the modern table lies in its two- or even three-dimensional display of all the known elements (and even the ones yet to be discovered) in a logical system of precisely ordered rows and columns.

In an early attempt to organize the elements into a meaningful array, German chemist Johann Döbereiner pointed out in 1817 that many of the known elements could be arranged by their similarities into groups of three, which he called triads. Döbereiner singled out triads of the elements lithium, sodium and potassium as well as chlorine, bromine and iodine. He noticed that if the three members of a triad were ordered according to their atomic weights, the properties of the middle element fell in between those of the first and third elements. For example, lithium, sodium and potassium all react vigorously with water. But lithium, the lightest of the triad, reacts more mildly than the other two, whereas the heaviest of the three, potassium, explodes violently. In addition, Döbereiner showed that the atomic weight of the middle element is close to the average of the weights for the first and third members of the triad.

Döbereiner's work encouraged others to search for correlations between the chemical properties of the elements and their atomic weights. One of those who pursued the triad approach further during the 19th century was Peter Kremers of Cologne, who suggested that certain elements could belong to two triads placed perpendicularly. Kremers thus broke new ground by comparing elements in two directions, a feature that later proved to be an essential aspect of Mendeleev's system.

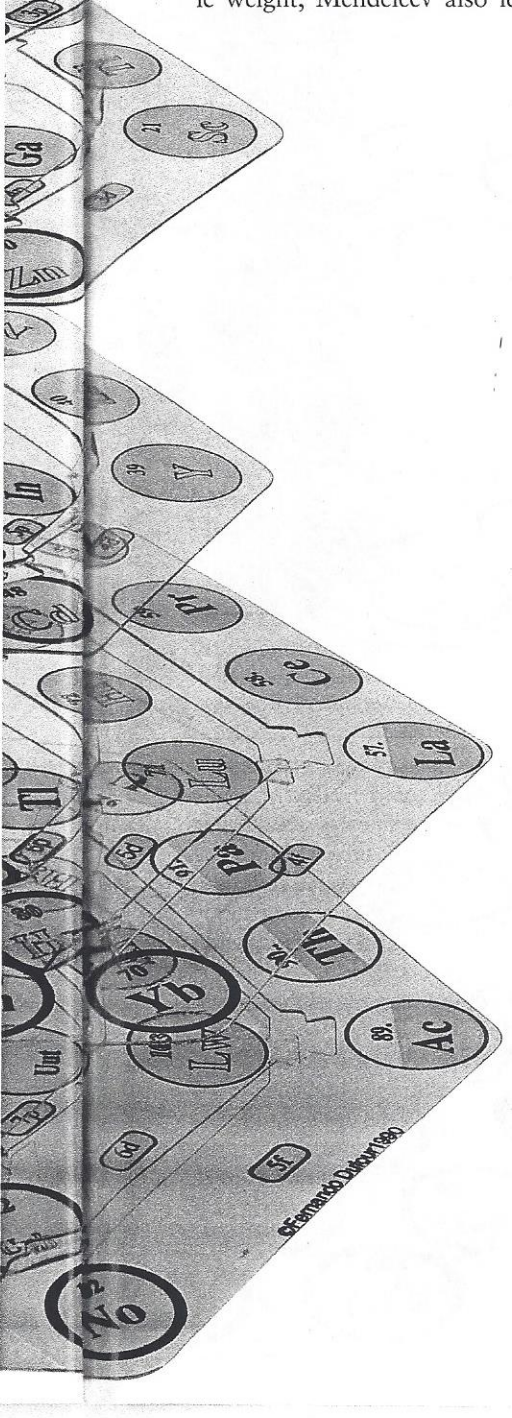
In 1857 French chemist Jean-Baptiste-André Dumas turned away from the idea of triads and focused instead on devising a set of mathematical equations that could account for the increase in atomic weight among several groups of chemically similar elements. But as chemists now recognize, any attempt to establish an organizing pattern based on an element's atomic weight will not succeed, because atomic weight is not the fundamental property that characterizes each of the elements.

Periodic Properties

The crucial characteristic of Mendeleev's system was that it illustrated a periodicity, or repetition, in the properties of the elements at certain regular intervals. This feature had been observed previously in an arrangement of elements by atomic weight devised in 1862 by French geologist Alexandre-Emile Béguyer de Chancourtois. The system relied on a fairly intricate geometric configuration: de Chancourtois positioned the elements according to increasing atomic weight along a spira[l] inscribed on the surface of a cylinder and inclined at 45 degrees from the base [*see illustration on next page*].

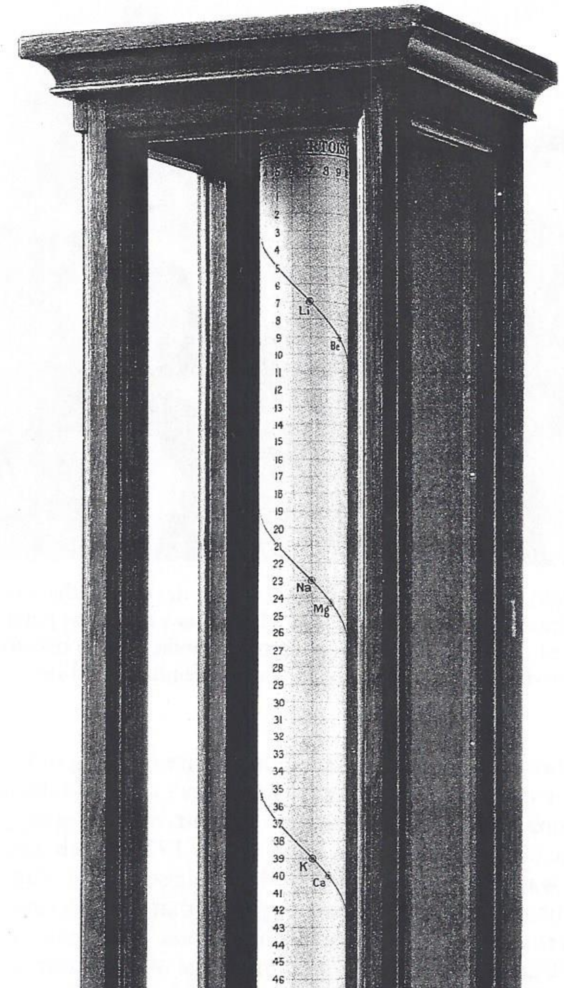
The first full turn of the spiral coincided with the element oxygen, and the second full turn occurred at sulfur. Elements that lined up vertically on the surface of the cylinder tended to have similar properties, so this arrangement succeeded in capturing some of the patterns that would later become central to Mendeleev's system. Yet for a number of reasons, de Chancourtois's system did not have much effect on scientists of the time: his original article failed to include a diagram of the table, the system was rather complicated, and the chemical similarities among elements were not displayed very convincingly.

Several other researchers put forward



DAN WAGNER

THREE-DIMENSIONAL TABLE transforms the traditional periodic chart into a multilayered structure. The traditional vertical columns, which correspond to a group or family of elements, can be seen running down the central core of this structure (for example, H, Li, Na and so on) as well as through the layers. Elements that are positioned on top of one another in layers, such as He, Ne, Ar and so on, belong in the sar[me] group and thus have similar chemical properties. The horizontal rows, or periods, [o]f the traditional table correspond to the multiple layers of the three-dimensional table. This version highlights the symmetrical and regularly increasing size of periods, a fundamental chemical feature not yet fully explained by quantum mechanics.



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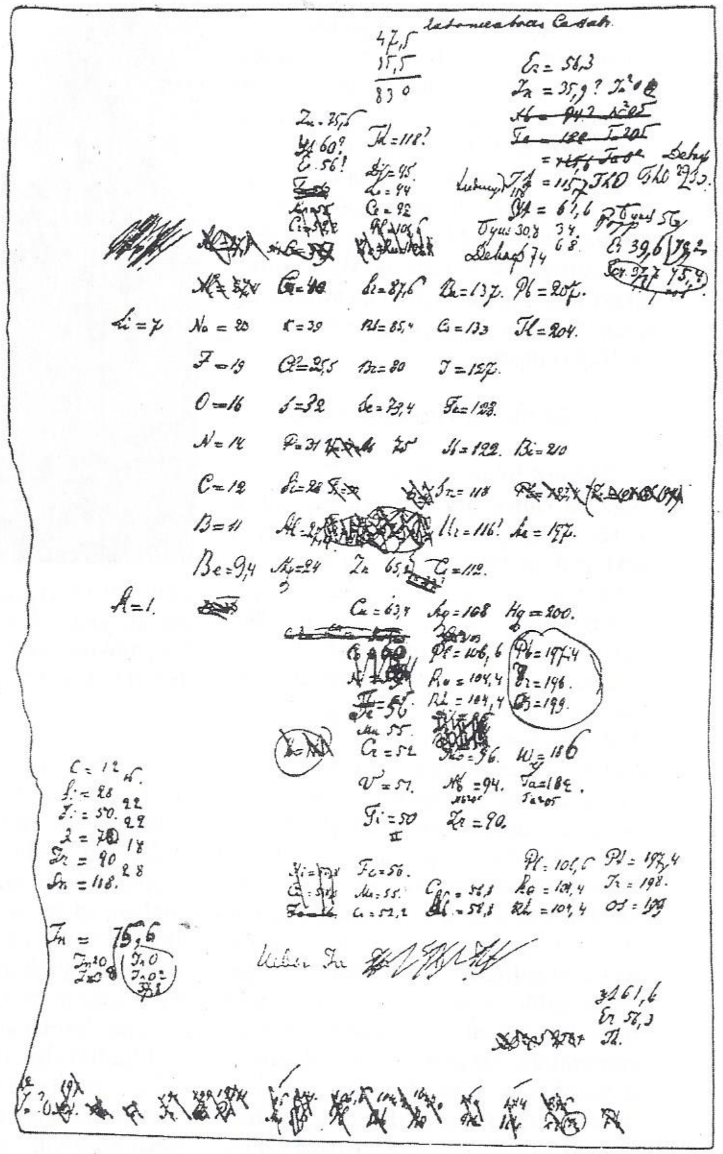
EARLY VERSION of an organizing system for the known elements was designed in 1862 by French geologist Alexandre-Emile Béguyer de Chancourtois. Known as the telluric screw, it was the earliest discovery of chemical periodicity.



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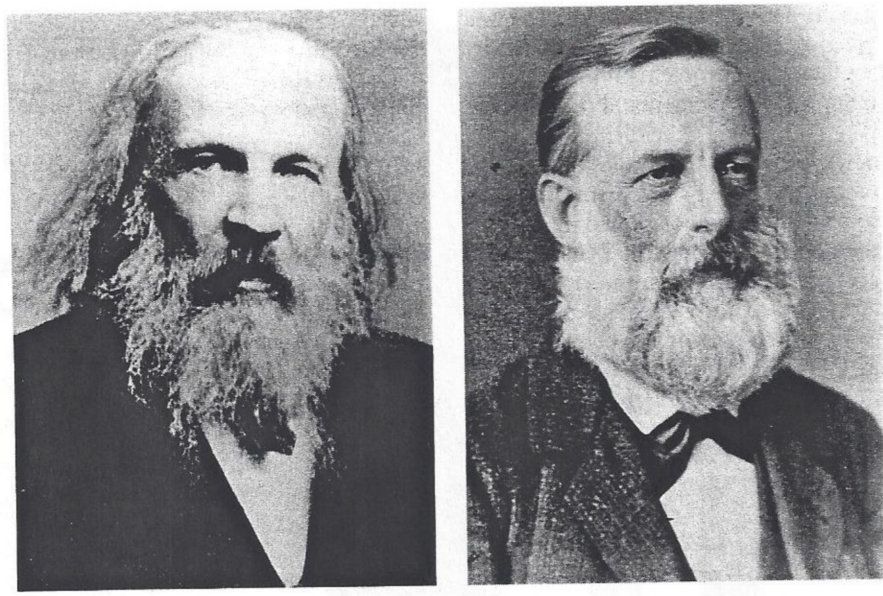
FIRST PERIODIC TABLE was developed by Russian chemist Dimitri Ivanovich Mendeleev in February 1869. This draft shows groups of elements arranged horizontally rather than in the more familiar vertical columns. Mendeleev produced many tables of both kinds.

their own versions of a periodic table during the 1860s. Using newly standardized values for atomic weights, English chemist John Newlands suggested in 1864 that when the elements were arranged in order of atomic weight, any one of the elements showed properties similar to those of the elements eight places ahead and eight places behind in the list—a feature that Newlands called "the law of octaves."

In his original table, Newlands left empty spaces for missing elements, but his more publicized version of 1866 did not include these open slots. Other chemists immediately raised objections to the table because it would not be able to accommodate any new elements that might be discovered. In fact, some investigators openly ridiculed Newlands's ideas. At a meeting of the Chemical Society in London in 1866, George Carey Foster of University College London asked Newlands whether he had considered ordering the elements alphabetically, because any kind of arrangement would present occasional coincidences. As a result of the meeting, the Chemical Society refused to publish Newlands's paper.

Despite its poor reception, however,

Newlands's work does represent the first time anyone used a sequence of ordinal numbers (in this case, one based on the sequence of atomic weights) to organize the elements. In this respect, Newlands anticipated the modern organization of the periodic table, which is based on the sequence of so-called atomic numbers. (The concept of atomic number, which indicates the number of protons present within an atom's nucleus, was not established until the early 20th century.)



CHEMISTS Mendeleev (*left*) and Julius Lothar Meyer (*right*) developed the modern periodic chart almost simultaneously in the late 1860s. Mendeleev's table was published first, and he receives most of the credit for discovering the periodic system because he used it to make many successful predictions and vigorously defended its validity.

CORBIS-BETTMANN (*left*); VAN PELT-DIETRICH LIBRARY, UNIVERSITY OF PENNSYLVANIA (*right*)

The Modern Periodic Table

Chemist Julius Lothar Meyer of Breslau University in Germany, while in the process of revising his chemistry textbook in 1868, produced a periodic table that turned out to be remarkably similar to Mendeleev's famous 1869 version—although Lothar Meyer failed to classify all the elements correctly. But the table did not appear in print until 1870 because of a publisher's delay—a factor that contributed to an acrimonious dispute for priority that ensued between Lothar Meyer and Mendeleev.

Around the same time, Mendeleev assembled his own periodic table while he, too, was writing a textbook of chemistry. Unlike his predecessors, Mendeleev had sufficient confidence in his periodic table to use it to predict several new elements and the properties of their compounds. He also corrected the atomic weights of some already known elements. Interestingly, Mendeleev admitted to having seen certain earlier tables, such as those of Newlands, but claimed to have been unaware of Lothar Meyer's work when developing his chart.

Although the predictive aspect of Mendeleev's table was a major advance, it seems to have been overemphasized by historians, who have generally suggested that Mendeleev's table was accepted especially because of this feature. These scholars have failed to notice that the citation from the Royal Society of London that accompanied the Davy Medal (which Mendeleev received in 1882) makes no mention whatsoever of his predictions. Instead Mendeleev's ability to accommodate the already known elements may have contributed as much to the acceptance of the periodic system as did his striking predictions. Although numerous scientists helped to develop the periodic system, Mendeleev receives most of the credit for discovering chemical periodicity because he elevated the discovery to a law of nature and spent the rest of his life boldly examining its consequences and defending its validity.

Defending the periodic table was no simple task—its accuracy was frequently challenged by subsequent discoveries. One notable occasion arose in 1894, when William Ramsay of University College London and Lord Rayleigh (John William Strutt) of the Royal Institution in London discovered the element argon; over the next few years, Ramsay announced the identification of four other elements—helium, neon, krypton and xenon—known as the noble gases. (The last of the known noble gases, radon, was discovered in 1900 by German physicist Friedrich Ernst Dorn.)

The name "noble" derives from the fact that all these gases seem to stand apart from the other elements, rarely interacting with them to form compounds. As a result, some chemists suggested that the noble gases did not even belong in the periodic table. These elements had not been predicted by Mendeleev or anyone else, and only after six years of intense effort could chemists and physicists successfully incorporate the noble gases into the table. In the new arrangement, an additional column was introduced between the halogens (the gaseous elements fluorine, chlorine, bromine, iodine and astatine) and the alkali metals (lithium, sodium, potassium, rubidium, cesium and francium).

A second point of contention surrounded the precise ordering of the elements. Mendeleev's original table positioned the elements according to atomic weight, but in 1913 Dutch amateur theoretical physicist Anton van den Broek suggested that the ordering principle for the periodic table lay instead in the nuclear charge of each atom. Physicist Henry Moseley, working at the University of Manchester, tested this hypothesis, also in 1913, shortly before his tragic death in World War I.

Moseley began by photographing the x-ray spectrum of 12 elements, 10 of which occupied consecutive places in the periodic table. He discovered that the frequencies of features called K-lines in the spectrum of each element were directly proportional to the squares of the integers representing the position of each successive element in the table. As Moseley put it, here was proof that "there is in the atom a fundamental quantity, which increases by regular steps as we pass from one element to the next." This fundamental quantity, first referred to as atomic number in 1920 by Ernest Rutherford, who was then at the University of Cambridge, is now identified as the number of protons in the nucleus.

Moseley's work provided a method that could be used to determine exactly how many empty spaces remained i the periodic table. After this discovery, chemists turned to using atomic number as the fundamental ordering principle for the periodic table, instead of atomic weight. This change resolved many of the lingering problems in the arrangement of the elements. For example, when iodine and tellurium were ordered according to atomic weight (with iodine first), the two elements appeared to be incorrectly positioned in terms of their chemical behavior. When ordered according to atomic number (with tellurium first), however, the two elements were in their correct positions.

Understanding the Atom

The periodic table inspired the work not only of chemists but also of atomic physicists struggling to understand the structure of the atom. In 1904, working at Cambridge, physicist J. J. Thomson (who also discovered the electron) developed a model of the atom, paying close attention to the periodicity of the elements. He proposed that the atoms of a particular element contained a specific number of electrons arranged in concentric rings. Furthermore, according to Thomson, elements with similar configurations of electrons would have similar properties; Thomson's work thus provided the first physical explanation for the periodicity of the elements. Although Thomson imagined the rings of electrons as lying inside the main body of the atom, rather than circulating around the nucleus as is believed today, his model does represent the first time anyone addressed the arrangement of electrons in the atom, a concept that pervades the whole of modern chemistry.

Danish physicist Niels Bohr, the first to bring quantum theory to bear on the structure of the atom, was also motivated by the arrangement of the elements in the periodic system. In Bohr's model of the atom, developed in 1913, electrons inhabit a series of concentric shells that encircle the nucleus. Bohr reasoned that elements in the same group of the periodic table might have identical configurations of electrons in their outermost shell and that the chemical properties of an element would depend in large part on the arrangement of electrons in the outer shell of its atoms.

Bohr's model of the atom also served to explain why the noble gases lack reactivity: noble gases possess full outer shells of electrons, making them unusually stable and unlikely to form compounds. Indeed, most other elements form compounds as a way to obtain full outer electron shells. More recent analysis of how Bohr arrived at these electronic configurations suggests that he functioned more like a chemist than has generally been credited. Bohr did not derive electron configurations from quantum theory but obtained them from the known chemical and spectroscopic properties of the elements.

In 1924 another physicist, Austrian-born Wolfgang Pauli, set out to explain the length of each row, or period, in the table. As a result, he developed the Pauli Exclusion Principle, which states that no two electrons can exist in exactly the same quantum state, which is defined by what scientists call quantum numbers. The lengths of the various periods emerge from experimental evidence about the order of electron-shell filling and from the quantum-mechanical restrictions on the four quantum numbers that electrons can adopt.

The modifications to quantum theory made by Werner Heisenberg and Erwin Schrödinger in the mid-1920s yielded quantum mechanics in essentially the form used to this day. But the influence of these changes on the periodic table has been rather minimal. Despite the efforts of many physicists and chemists, quantum mechanics cannot explain the periodic table any further. For example, it cannot explain from first principles the order in which electrons fill the various electron shells. The electronic configurations of atoms, on which our modern understanding of the periodic table is based, cannot be derived using quantum mechanics (this is because the fundamental equation of quantum mechanics, the Schrödinger equation, cannot be solved exactly for atoms other than hydrogen). As a result, quantum mechanics can only reproduce Mendeleev's origi-

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	71 Lu	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	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110*	111*	112*	113†	114†	115†	116†	117†	118†

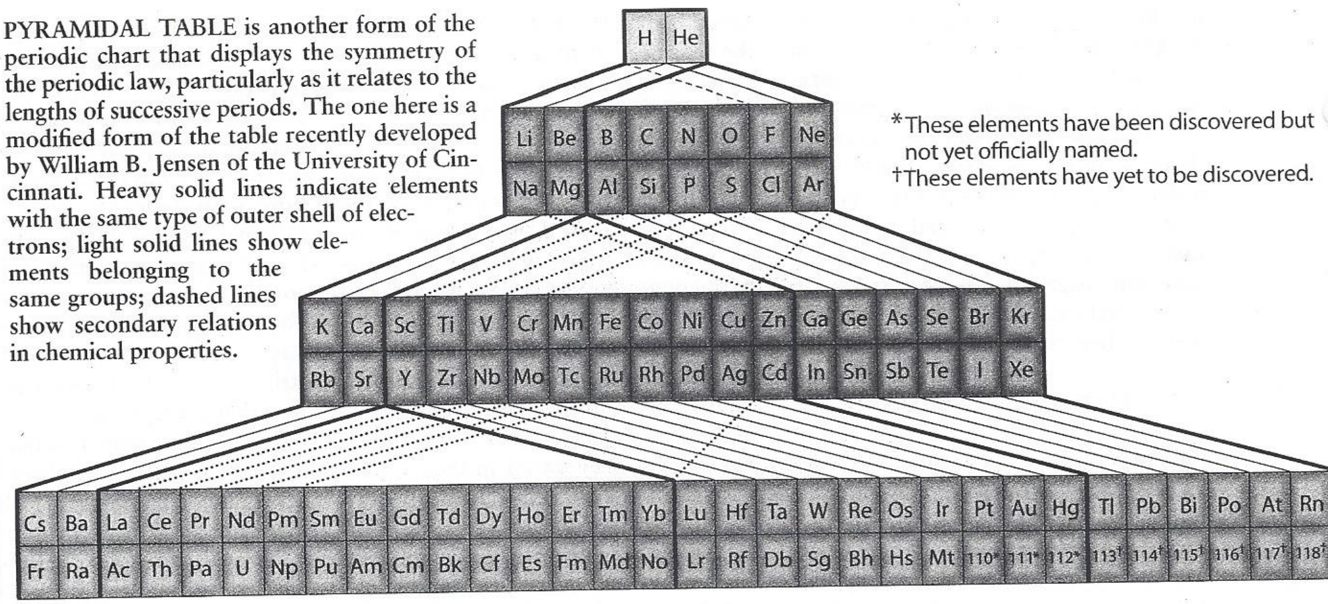
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Td	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

*These elements have been discovered but not yet officially named.
†These elements have yet to be discovered.

POPULAR PERIODIC TABLE—known as the medium-long form—can be found in nearly every chemistry classroom and laboratory around the world. This version has the advantage of clearly displaying groups of elements that have similar chemical properties in vertical columns, but it is not particularly symmetrical. (The different colors of the table indicate elements with the same type of outer shell of electrons.)

LAURIE GRACE

PYRAMIDAL TABLE is another form of the periodic chart that displays the symmetry of the periodic law, particularly as it relates to the lengths of successive periods. The one here is a modified form of the table recently developed by William B. Jensen of the University of Cincinnati. Heavy solid lines indicate elements with the same type of outer shell of electrons; light solid lines show elements belonging to the same groups; dashed lines show secondary relations in chemical properties.



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LAURIE GRACE

nal discovery by the use of mathematical approximations—it cannot predict the periodic system.

Variations on a Theme

In more recent times, researchers have proposed different approaches for displaying the periodic system. For instance, Fernando Dufour, a retired chemistry professor from Collège Ahuntsic in Montreal, has developed a three-dimensional periodic table, which displays the fundamental symmetry of the periodic law, unlike the common two-dimensional form of the table in common use. The same virtue is also seen in a version of the periodic table shaped as a pyramid, a form suggested on many occasions but most recently refined by William B. Jensen of the University of Cincinnati [*see illustration above*].

Another departure has been the invention of periodic systems aimed at summarizing the properties of compounds rather than elements. In 1980 Ray Hefferlin of Southern Adventist University in Collegedale, Tenn., devised a periodic system for all the conceivable diatomic molecules that could be formed between the first 118 elements (only 112 have been discovered to date).

Hefferlin's chart reveals that certain properties of molecules—the distance between atoms and the energy required to ionize the molecule, for instance—occur in regular patterns. This table has enabled scientists to predict the properties of diatomic molecules successfully.

In a similar effort, Jerry R. Dias of the University of Missouri at Kansas City devised a periodic classification of a type of organic molecule called benzenoid aromatic hydrocarbons. The compound naphthalene ($C_{10}H_8$), found in mothballs, is the simplest example. Dias's classification system is analogous to Döbereiner's triads of elements: any central molecule of a triad has a total number of carbon and hydrogen atoms that is the mean of the flanking entries, both downward and across the table. This scheme has been applied to a systematic study of the properties of benzenoid aromatic hydrocarbons and, with the use of graph theory, has led to predictions of the stability and reactivity of some of these compounds.

Still, it is the periodic table of the elements that has had the widest and most enduring influence. After evolving for over 200 years through the work of many people, the periodic table remains at the heart of the study of chemistry. It ranks as one of the most fruitful ideas in modern science, comparable perhaps to Charles Darwin's theory of evolution. Unlike theories such as Newtonian mechanics, it has not been falsified or revolutionized by modern physics but has adapted and matured while remaining essentially unscathed. SA

The Author

ERIC R. SCERRI studied chemistry at the universities of London, Cambridge and Southampton. He later earned a Ph.D. in history and philosophy of science from King's College, London. Since arriving in the U.S., he has been a research fellow at the California Institute of Technology and, most recently, has taught chemistry at Bradley University in Peoria, Ill. In January 1999 he will take up a position in the chemistry department at Purdue University. Scerri's research interests lie in the history and philosophy of chemistry, and he is the editor of the interdisciplinary journal *Foundations of Chemistry* (http://www.cco.caltech.edu/~scerri/ on the World Wide Web). His e-mail address is scerri@bradley.edu

Further Reading

THE PERIODIC SYSTEM OF CHEMICAL ELEMENTS: A HISTORY OF THE FIRST HUNDRED YEARS. J. W. van Spronsen. Elsevier, 1969.

THE SURPRISING PERIODIC TABLE: TEN REMARKABLE FACTS. Dennis H. Rouvray in *Chemical Intelligencer,* Vol. 2, No. 3, pages 39–47; July 1996.

CLASSIFICATION, SYMMETRY AND THE PERIODIC TABLE. William B. Jensen in *Computing and Mathematics with Applications,* Vol. 12B, Nos. 1–2, pages 487–510; 1989.

PLUS ÇA CHANGE. E. R. Scerri in *Chemistry in Britain,* Vol. 30, No. 5, pages 379–381; May 1994. (Also see related articles in this issue.)

THE ELECTRON AND THE PERIODIC TABLE. Eric R. Scerri in *American Scientist,* Vol. 85, pages 546–553; November–December 1997.

For information on Fernando Dufour's three-dimensional periodic table, send e-mail to fernduf@aei.ca