The Periodic Table: Looking Forward Gary Katz Periodic Round Table

The Periodic Table is a familiar sight in textbooks and classrooms around the world – the icon of chemistry. Except for the addition of elements heavier than uranium, it has not changed in more than fifty years. This apparent stability does not mean that the evolution of the Periodic Table is complete. Advanced perspectives on the lightest elements, as well as progress in synthesizing ever heavier elements may imply that a change in the shape of the table will be necessary. This will be a normal event in the history of the Table, as it has already changed shape a great deal in the course of its development.

The story of the Periodic Table is a large part of the evolving story of chemistry over the last two hundred years. In order for the periodic system to begin to develop, the basic language of chemistry had to be invented. Words like "element", "compound", "atom", and "atomic weight" had to be created and put to use. Roman letters replaced the arcane glyphs of alchemy as symbols of the elements

In addition, the rules of chemical interaction had to be devised, among them the law of conservation of matter, the laws of definite and multiple proportions, and the gas law of combining volumes. Much of this task was accomplished during the period 1705 – 1815 by early chemists like Antoine Lavoisier and John Dalton, now considered the most prominent organizers of modern chemistry. By1817, fifty-two elements were known- including twenty discovered in the busy first years of the nineteenth century.

Chemistry was still an inexact science. For years chemists remained in confusion over whether hydrogen and oxygen were monatomic or diatomic; or whether the correct formula for water was HO, or something else (the formula H2O was not verified until much later in the century. Working with the abundant supply of elements, chemists were able to determine that each element had a characteristic atomic weight, which allowed the ordering of elements by size. In 1816 the Scottish physician William Prout observed that almost all atomic weights were integers, starting with hydrogen, which by convention had an atomic weight of one. Prout hypothesized that all the elements were multiples of the hydrogen atom; prophetically, he called this fundamental unit the "protyle". Nearly one hundred years later, in 1915, Henry Moseley elucidated the existence of the atomic numbers, thus turning protyles into protons. Until Moseley's discovery, chemists had to make do with atomic weights, which caused numerous difficulties later on in the development of the Periodic Table.

The arrangement of the elements by size resulted in a list of elements progressing from

small (hydrogen) to larger (gold, lead, even uranium) in a one-dimensional order. But it became known quite early that certain elements shared common chemical and physical properties, i.e. displayed a family resemblance. This was most apparent among what are now known as the group one and two elements, but was also seen in halogens and metals. Johann Dobereiner, a German chemist, found in 1817 that in a few cases, a series of three similar elements had an unusual numerical relationship in which the atomic weight of the middle element was the mathematical average of the lighter and heavier elements, a relationship called a triad.

The first of Dobereiner's triads consisted of the elements calcium, strontium and barium, and numerous other triads followed - about ten in all. However, only certain groups of three similar elements form triads - something that puzzled the nineteenth century chemists. Looking at the modern day periodic table, it is easy to see why; a triad forms only where the periods bracketed by the three elements of a triad are the same length. We now know that the periods are of quite different lengths. The true shape of the Periodic Table would not be revealed until the twentieth century.

Whatever their shortcomings, enough triads were found to indicate that the elements might be organized according to some kind of mathematical plan. To the idea that elements could be listed in order of size was added a second concept; that certain specific properties recurred on a regular or periodic basis, giving chemists an incentive to search for an organizational scheme in two dimensions that would accommodate the family resemblances and triads. The nineteenth century saw the rapid rise of chemical research in Europe, as new elements gave rise to new reactions, amid growing confusion about the meaning of this proliferation of "primary substances". Robert Bunsen's discovery of flame spectroscopy in the 1850s made it much easier to detect and separate new elements. In 1860, convinced of the need to share chemical knowledge, several leading German chemists organized the world's first international chemistry conference at Karlsruhe, Germany, attended by chemists from all the European countries and even Mexico. At this historic event, Stanislao Cannizzaro presented highly accurate new values for the atomic weights that would prove essential to the task of to determining the proper order of the elements.

In the decade following Karlsruhe no fewer than six chemists published two-dimensional graphic displays of the elements that qualify as forerunners of the present day Periodic Table. A Russian, Dmitri Mendeleev, and a German, J. Lothar Meyer, produced the most successful of these first true periodic tables in the interval 1869-1871. Though both claimed ownership of the concept, Mendeleev is generally credited with being the winner in the priority dispute. Not only did he coin the term "periodic system", he also successfully predicted that three new elements would be discovered to fill spaces that appeared in his table. Mendeleev wrote an important chemistry textbook featuring the concept of the periodic law that was translated into numerous languages.

Though it is hard to believe today, acceptance of the Periodic Table was not immediate in all quarters, and Mendeleev continued to work for its advancement until his death in 1907. Some issues were not resolved in his lifetime that contributed to skepticism about the Periodic System. Among them were the puzzling rare-earths, whose position in the table was difficult to interpret, and the troubling cases where the atomic weight order seemed to be violated by reversed element-pairs like tellurium-iodine and cobalt-nickel. Resolution of these old problems and new ones, like what to do with the inert gases, would await the beginning of the twentieth century and the arrival of atomic and nuclear physics.

A flood of new developments at the end of the nineteenth century challenged the concepts behind the Periodic Table. First, William Ramsay and others discovered six new inert gases in six years (1895-1900). Without valence and unable to combine with other elements, these gaseous new elements befuddled the chemists and resisted placement in the Table. Then came the revelation that atoms consisted of even smaller nuclei surrounded by tiny electrons in largely empty space. Finally, the perplexing phenomena of radioactivity and radiation seemed to contradict the longstanding principle of the immutability of elements.

By the twentieth century, there were seven blank spaces left to fill in the table; only three of these would be filled by stable elements found in nature. This immense task had been achieved through traditional chemistry, but that phase in the evolution of the Periodic Table was ending, and a new phase began dominated by the techniques of physics. The study of radioactivity and radiation at the laboratory of Pierre and Marie Curie revealed the existence of a large number of radioactive species. Could these all be new elements?

Frederick Soddy, an associate of Lord Rutherford in England, after years of painstaking chemical separation, showed that numerous versions of an element could exist, each differing in atomic weight but not in chemical properties. These versions Soddy called isotopes, meaning they shared the same place in the Periodic Table. This finding explained why atomic weights had not proved satisfactory in ordering the element.

In 1916, Henry Moseley, also associated with Rutherford, demonstrated that the order of the elements exactly followed increasing positive charge in the nucleus. Moseley introduced the concept of atomic number as the equivalent of the nuclear charge, and he determined that the elements followed an exact integral order when atomic number served as the organizing principle. Moseley was ably to place the lanthanide elements in the correct order, resolving the question of how many of these hard-to-separate elements there were. He clearly showed the absence of elements at Z=43 and Z=61: these elements would be found in nuclear reactor products much later.

While Moseley developed the idea of atomic number, Niels Bohr, a young Danish physicist also working with the Rutherford group, concentrated on the role of the electrons. Earlier, Rutherford had shown experimentally that electrons of an atom occupy a relatively large empty space around the small dense nucleus. Bohr set out to describe theoretically just what these electrons were doing out there, choosing as his model the hydrogen atom with its single electron. Envisioning the atom as a planetary system with the electron orbiting the nucleus, Bohr proposed that the electronic orbits were quantized, that is could have only specific allowed values, in accord with the quite new quantum theory of Planck and Einstein.

Following an interruption of some years caused by WWI, Bohr expanded the scope to characterize the electronic structure of the heavier elements. Using the Periodic Table itself as a model for the electronic structure of the atom, Bohr and others placed the electrons in successive "orbitals" of specific allowed energy levels. As atomic number increased, the electronic configuration of the atom was built up one electron at a time.

The relationship between the Periodic Table and the system of electronic configuration is so close that they are virtually the same system. Why then, one might ask, doesn't the electronic configuration system correspond more exactly to the Periodic Table? In fact, Charles Janet, a retired French scientist constructed a series of such tables in 1928. Janet's basic electronic configuration table, or eight-period table, appears in figure 1, and differs from the standard table in subtle ways that markedly enhance the informational content of the Periodic Table.

The standard Table reads from left to right, with the orbital sections in the order s, f, d, p, (fig.2). Now move the s column from the left side to the right and shift it up one block: the s elements are now on the right side of the table, though it still reads from left to right. Helium is then moved from the inert gases to the top of the first period, next to hydrogen, as they both share a 1s configuration.

In the eight-period table the orbitals appear in the order s, p, d, f, going from right to left, while the elements still are in sequence from left to right (fig. 1). The periods have now been renumbered. Except for the s elements, the enumeration of the periods increases by one unit, so that former period three is now four, six is now seven, and so on. The composition of all groups remains the same (except for helium); only the periods have been changed.

The orbital map (fig.3) shows that each period now consists of elements whose (n + 1) sums add up to the ordinal number of the period. (n and I) are the first two quantum numbers of the differentiating electron of an element. The differentiating electron is the one that distinguishes an element from the one before it in the table, which has atomic number one less. The differentiating electron is the one that uniquely determines the properties of a given element. The sum (n + 1) can be thought of as the energy level of the elements on a particular line. So, for example, in period seven, four orbitals with the (n + 1) sums 7 + 0 (7s); 6 + 1(6p); 5 + 2 (5d); 4 + 3 (4f), all equal to seven.

The eight-period table possesses a mathematical regularity that was not present in the standard version. Some of the features of the new arrangement are:

- 1) The eight periods occur as four pairs of two periods of equal length
- 2) Number of elements in periods equals 2n[squared} where n = 0, 1,2,3,4: actual population of elements 2, 2, 8, 8, 18, 18, 32, 32
- 3) Number of elements in period also equals sum of orbital populations, i.e. 2 + 6 + 10 + 14 . . . (this is twice the series of odd numbers)
- 4) (n + I) = P which is the mathematical form of the Periodic Law

Several commentators have said that the term "Periodic Law" (a favorite of Mendeleev) is obsolete and incorrect. That perception however may stem from the use of a periodic table that is faulty. Mendeleev was right - there is a Periodic Law!

The eight-period table is the basis for the four tiered, three-dimensional, solid Periodic Round Table (fig. 4). This symmetrical expansion of the Periodic Law displays the elements in tangible form on four pairs of discs. Importantly, the lanthanide and actinide elements form the outer rings of the basal discs (fig. 5), where they are an integral part of the Table, not a footnote.

IUPAC (International Union of Pure and Applied Chemistry) officially controls the structure of the Periodic Table, while an organization of physicists, the International Union of Pure and Applied Physics (IUPAP), has a somewhat subordinate role. Presently, IUPAC approves only the seven-period table, and no effort has yet been undertaken to submit proposals for change.

The chief objection to the EC tables has been that helium should not be classed among the s2 elements because it is an inert gas, not a group two alkali metal. This objection overlooks the fact that when placed with the p6 inert gases, helium is the only element on the chart that is not grouped with elements of the same orbital designation. People have also disagreed about the placement of the first element, hydrogen. With its 1s electron, hydrogen has usually been grouped with the s elements.

Hydrogen and helium are now known to play a unique role in the formation of the other elements. They react in stars through nuclear fusion to form the higher elements, a process called nucleosynthesis, which has become fairly well understood in only the last fifty years. As the universal progenitors of the higher elements, hydrogen and helium have a unique status that may qualify them to occupy a separate island above the s column. This graphic indicates that they share the group's electronic configuration, but not necessarily the chemical/physical properties of the group.

Fifty years ago, the frontier of the Periodic Table was growing rapidly through the addition of the man-made synthetic elements. From 1940 to 1960 the team of Glenn T. Seaborg at Berkeley created ten new elements heavier than uranium – the transuranium elements – completing the actinide series. In 1946, Seaborg proposed that the sequence of transuranium elements in the actinide series constituted a series homologous to the lanthanides, as predicted by the Janet table.

The Berkeley research effort subsequently produced elements beyond the actinide series, now called the transfermium elements (even though fermium, element 100, is actually in the actinide series). The transfermium elements extend the actinide series under the main body of the Table progressively filling the rest of period eight (period seven of the standard version), through the 6d and 7p orbitals.

New elements continue to be synthesized at this active frontier of the Periodic Table. Elements 110 and 111 have been recently named in this decade. Researchers at four accelerator facilities around the world are producing heavier nuclei of elements up to 118 . . . and beyond. Typically these atoms are very unstable with short half lives to nuclear disintegration under terrestrial conditions

Heavy elements are also being studied theoretically using computer models that mathematically simulate the atomic structure of a hypothetical element to predict its chemical and physical properties. Such studies have been published for element 126, which would be located in the 5g orbital of the ninth period. But there is no provision for expansion of the sevenperiod table, as the format ends at element 118. The electronic configuration table is, however, infinitely expandable. Periods nine and ten, with fifty elements each, can easily be added to the base of the Table. Since there is no natural limit to the number of elements, the format of the Periodic table must be infinitely expandable.

When combined fully with the system of electronic configuration, the Periodic Table conforms to the Periodic Law. The difference between the eight-period table and the IUPAC standard table consists of a small shift in position, yet the rewards are substantial. An electronic configuration table also provides the best format for depicting the lanthanide/actinide groups as well as displaying future very heavy elements.

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Guide to Figures

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