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A Book Collector's View of the Periodic Table: Key Documents before Mendeleev's Contributions of 1869

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Abstract. The present article identifies and discusses some of the books and scientific articles that played important roles in the development of the periodic law, before Mendeleev published his Periodic System in 1869. For each book, information is given about the edition in which the discovery was made, and for each scientific article, information is given about the form in which it was issued, such as whether offprints were printed in addition to the journal appearance. Some observations of interest to book collectors are included, such as assessments of the availability of these documents on the rare book market. This paper may also be of use to those who wish to learn about (or to teach) the history of the periodic law from the original documents that first announced important advances toward its creation.

Keywords. Periodic table, Mendeleev, chemical elements, rare books, offprints, bibliography.

INTRODUCTION

One of the most important unifying principles in all of science is the periodic law of the chemical elements. The history of the conception and development of the system and its associated periodic table is both rich and fascinating, and the books, monographs, and journal publications that led to its creation and improvement have been the subject of much study and commentary.¹⁻⁵

The purpose of the present article is to identify and discuss, from a book collector's perspective, some of publications that played important roles in the development of the periodic law. In the current paper, I will focus on those contributions that were made before Mendeleev published his breakthrough ideas beginning in 1869. Most of these documents appear only infrequently on the rare book market but can be acquired by the patient collector. This paper may also be of use to those who wish to learn about (or to teach) the history of the periodic law from the original documents that first announced important advances toward its creation.

BOYLE'S DEFINITION OF AN ELEMENT (1661).

The book *The Sceptical Chymist: or Chymico-Physical Doubts and Paradoxes*⁶ by the Anglo-Irish natural philosopher Robert Boyle (1627-1691) is an appropriate place to start because it contains early speculations about the basic particles of matter. In this book (Fig. 1), Boyle presented his theory that matter consists of a hierarchical arrangement of particles, and defined elements as “certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved.”

Of the books mentioned in the current paper, the *Sceptical Chymist* is one of the rarest. In a census carried out in 1960, only 27 copies of the first (1661) edition could be located, and 5 others previously known to be in private collections could not be traced.⁷ My own efforts to update the census suggests that perhaps 65 copies exist, of which perhaps six are privately held. These are very small numbers even for a seventeenth century book.

Some variants of the first edition of the *Sceptical Chymist* are known. The leaf bearing pages 243 and 244 is found in two states: about 20% of the known copies have the leaf in its original state (in which a part of a sentence is inadvertently printed twice) and most of the rest contain a replacement leaf that corrected the error. In addition, about 20% of the known copies lack the four-page list of errata that usually appears at the end of the text. Copies without the errata more likely to have the original leaf, and copies with the errata are more likely to have replacement leaf. These correlations suggest that the addition of both the replacement leaf and the errata occurred sometime after the book was printed, but before all the copies had been bound and sold.

The second English edition of the *Sceptical Chymist* (Oxford, 1680) is nearly twice as long as the first edition because it contains much new material, under the subtitle *Experiments and Notes about the Producibleness of Chymical Principles*. Several Latin editions of the *Sceptical Chymist* were also printed. All of these later editions are also scarce, although not as rare as the first English edition, which is today almost impossible to collect.

LAVOISIER'S TABLE OF SIMPLE SUBSTANCES
(1787 AND 1789)

In 1787, the French chemist Antoine Laurent Lavoisier (1743-1794), along with three compatriots, Louis-Bernard Guyton de Morveau (1737-1816), Claude Louis

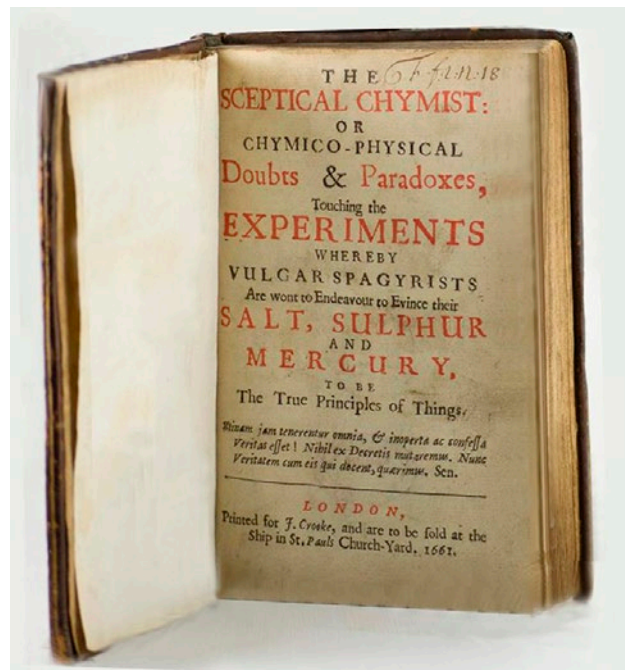


Figure 1. One of the two title pages in the first edition of Boyle's *Sceptical Chymist*, 1661. Only about 65 copies of this book are known, perhaps six of which are owned privately, the rest being in institutional libraries

Berthollet (1748-1822), and Antoine François de Fourcroy (1755-1809), published an important book, *Méthode de Nomenclature Chimique*,⁸ which grew out of a paper that had been written by Guyton de Morveau in 1782.⁹ This book introduced a new system of chemical nomenclature, still used today, in which names are based on the chemical content; for example, the substance the alchemists called “pompholix” is referred to instead as zinc oxide.

In the context of the development of the periodic table, the *Méthode* is notable for being one of the first to give a list of chemical elements, which the authors defined as substances that cannot be further decomposed. In Table II, the book gives a list that contains fifty-one “simple substances”. Of these, twenty-one were elements as we recognize them today (N, H, C, S, P, Au, Pt, Ag, Hg, Sn, Cu, Pb, Fe, Zn, Mn, Ni, Bi, Sb, As, Mo, W), seven were elements that they suspected were combined with oxygen (K, Na, Ba, Ca, Mg, Al, and Si), and three others were radicals that had not yet been isolated from their acids (Cl, B, and F). The remaining substances were the radicals of various organic acids, along with ether and alcohol.

Interestingly, two states of the first edition of the *Méthode* have been identified: in one, pages 257-272 are misnumbered 241-256; in the other, only half of these

pages are misnumbered. These states were once considered to be different issues of the first edition, meaning that they were printed and sold by the publisher at different times.¹⁰ It is more likely, however, that all of the first edition copies stem from the same print run, and that some of the page numbers were corrected partway through the printing but before the books were bound. Today, the two states of the *Méthode* are of equal value. The second edition, which was a page-for-page reprinting dated the same year, can be recognized because it bears a different figure on the title page (a vase of flowers instead of a cherub supervising a distillation) and it lacks the printer's colophon on p. 314.

Two years after the appearance of the *Méthode*, Lavoisier published his landmark textbook *Traité Élémentaire de Chimie, présenté dans un ordre nouveau et d'après les découvertes modernes...* [*Elementary Treatise on Chemistry, Presented According to a New Order and After the Modern Discoveries...*].¹¹ In this book, Lavoisier overthrew the phlogiston theory, emphasized the concept of the conservation of mass, and proved that the increase in the weight of calcined metals was due to something taken from the air, which had first been given the name "oxygen" in the *Méthode*. The *Traité* also contains a "Tableau des substances simples," which looks much more like a modern list of chemical elements: it repeats the list of simple substances given in the *Méthode*, but omits the organic radicals, ether, and alcohol. Lavoisier's list also includes light and heat among these substances; interestingly, he omitted the "fixed alkalies" potash and soda from this list because he believed them to be compounds of unknown composition.

The first edition of the *Traité Élémentaire de Chimie* is a relatively common book, and copies are regularly available for purchase. Most copies of the first edition consist of 653 pages, but before the publication of the full text of the first edition, Lavoisier had a small number of copies of the book bound in one volume of only 558 pages.¹⁰ This version lacks the "Tables à l'Usage des Chimistes," the "Table des Matières," and the approbation of the Académie des Sciences (dated 4 February 1789), which had not yet been printed. Although the 558-page version has been referred to as a first edition, and the regular 653 page version as a second edition,¹² they are more properly described as the first and second issues of the first edition.¹³

The first issue is most easily identified by the absence of the words "Tome Premier" on the half-title and title page; ten copies of the first issue are currently known. Four of these are bound in calf, three of which are in institutional libraries: the National Library of France (BNF, rebound), the Mazarine Library in Paris,

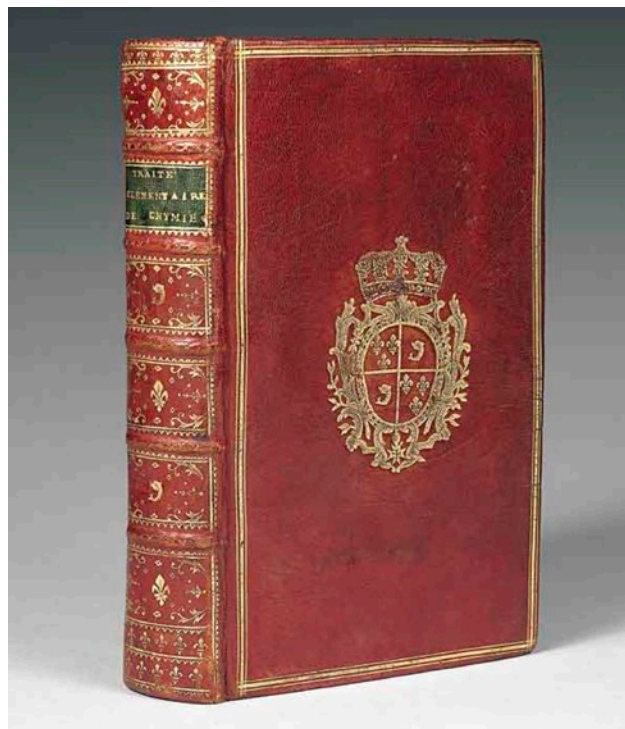


Figure 2. One of ten known 558-page first issues of Lavoisier's *Traité Élémentaire de Chimie*, 1789, in a presentation binding for the dauphin Louis-Joseph-François-Xavier de France, the eldest son of Louis XVI and Marie Antoinette, who died in June 1789 at the age of eight.

and Cornell University (Lavoisier's personal copy). The fourth known copy in calf was sold at auction in Paris in 2010.

The six other known copies were given to the Royal Family and were sumptuously bound in red morocco bearing the arms of the recipient in the center of each of the boards (Fig. 2). Five of these are in institutional libraries: that of Louis XVI at the Library of Versailles, that of Marie Antoinette at the BNF, that of Louis Stanislas Xavier de Bourbon, Count of Provence (later Louis XVIII) at the Sainte Geneviève Library, that of Charles Philippe of France, Count of Artois (later Charles X) at the Library of the Arsenal, and that of Marie-Thérèse de Savoie, Countess of Artois at the Institute of France. One other copy bound in red morocco was given to the eldest son of Louis XVI and Marie Antoinette, the dauphin Louis-Joseph-François-Xavier de France, who died in June 1789 at the age of eight; this copy sold at auction in Paris in 2005.

Several later editions of the *Traité Élémentaire* were published during Lavoisier's lifetime, and the book also appeared in English, Spanish, German, Italian, and Dutch translations

DALTON'S ATOMIC WEIGHTS (1805 AND 1808).

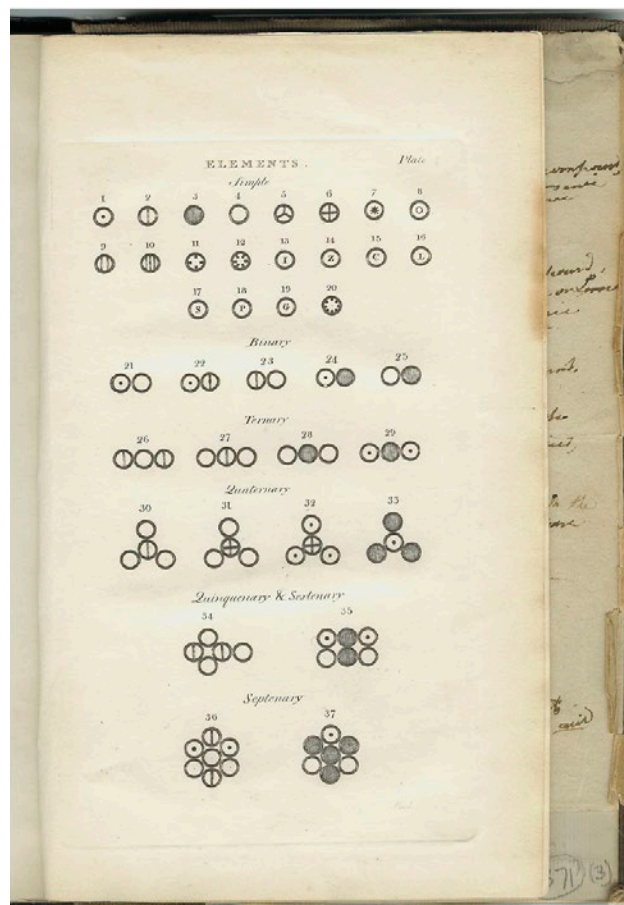
The English chemist John Dalton (1766-1844) is well known for his atomic theory of matter, in which he proposed that all atoms of a given element are identical in mass and properties. Dalton's atomic theory is important for several reasons: one is that it made it possible for the first time to devise chemical formulas for pure substances, and another is that it provided the first way to list the elements in an order that (eventually) would be used to uncover periodic relationships.

Dalton first proposed the idea that atoms of an element had a characteristic weight in a journal article he published in 1805 entitled "The Absorption of Gases by Water and Other Liquids."¹⁴ Dalton was led to this hypothesis during his research that showed that different gases were differently soluble in water: gases with low densities and only one kind of atom (such as hydrogen) were less soluble than gases with larger densities and more than one kind of atom (such as carbon dioxide). He proposed that the amount of gas that dissolves in water at a given gas pressure "depends upon the weight and number of the ultimate particles of the several gases, those whose particles are lightest and single being least absorbable and the others more, according as they increase in weight and complexity."

Without any further discussion, Dalton appended a table to his article, in which he listed his measurements of "the relative weights of the ultimate particles of gaseous and other bodies." His list is (mostly) in order of increasing weight, beginning with hydrogen (which he assigned a relative weight of 1) and continuing with 20 other substances, the one with the largest relative weight being sulfuric acid. Some of Dalton's numbers are molecular weights and some are atomic weights; among the latter are proposed values for H, N, C, O, P, and S, although none of the values matches modern atomic weights because Dalton made mostly incorrect assumptions about combining ratios.

Although most early scientific discoveries were first announced in books, from the 18th century onward it became increasingly common for new ideas to be presented as papers in scientific journals. Authors began requesting separate copies of their papers for them to distribute to scientific colleagues. Such authors' separates are known as "reprints" among practicing scientists but are called "offprints" in the book trade.¹⁵ As far as I know, however, no offprints of Dalton's 1805 article in the *Manchester Memoirs* exist; this document can be collected only as the journal issue or bound volume.

Dalton gave more information about his atomic ideas in his magnum opus, *New System of Chemical Phi-*



Joseph A. Ransome, Esq.
from John Dalton, M.L.S. &c.

Figure 3. Dalton's table of elements and compounds from the first volume of his *New System of Chemical Philosophy* (top). This copy also contains experimental notes in Dalton's handwriting (partially visible at right) as well as Dalton's handwritten inscription presenting this copy to his personal physician, Joseph A. Ransome (bottom).

losophy, published in three volumes between 1808 and 1827.¹⁶ The first of the three volumes was devoted almost entirely to a discussion of heat and the forces between chemical substances. Only in the last four pages of the first volume did Dalton turn to his atomic theory; he wrote, "Now it is one great object of this work, to shew the importance and advantage of ascertaining *the relative weights of the ultimate particles, both of simple and compound bodies...*" (italics in original). In one of the figures that appears after the end of the text (Fig. 3),

Dalton gave for the first time a table of the then-known elements arranged in order of increasing atomic weight; remarkably, the atomic weights themselves appear only in the caption to this figure!

Complete sets of all three volumes of Dalton's *New System* are hard to find on the collector's market, in part because few people who bought the first two volumes were persistent enough (and still alive) to purchase the third volume, which appeared nearly 20 years later.

AMPÈRE'S ATTEMPT TO CLASSIFY ELEMENTS (1816)

One of the earliest attempts to classify elements according to their chemical properties was devised by the French physicist André-Marie Ampère (1775-1836). In 1816, Ampère published a journal article, "Essai d'une classification naturelle pour les corps simples [Essay on a Natural Classification of the Elements],"¹⁷ in which he classified the elements according to their relative affinity for oxygen and the nature of the compounds they form with it. Ampère's system of classifying elements according to their chemical reactivity resembles the approach of Étienne François Geoffroy (1672-1731), who published the first table of relative chemical affinities in 1718.¹⁸ Like Mendeleev's periodic table, Ampère's system was intended to be an instrument of chemical research, and in fact it was still being used in the 1860s.¹⁹

Ampère commissioned offprints of his 1816 journal article, which are identifiable by the repagination of the two parts as pages 1-44 and 1-35. These offprints are quite scarce, however, with perhaps five or so copies still extant. Far more common is the 1816 journal volume of the *Annales de chimie et de physique* in which Ampère's paper appears.

DOBEREINER'S TRIADS (1817 AND 1829)

In 1817, the German chemist Johann Wolfgang Döbereiner (1780-1849) took one of the first steps towards the creation of the periodic table. In a letter sent in 1817 to *Annalen der Physik*, Döbereiner's colleague Ferdinand Wurzer (1765-1844) briefly reported Döbereiner's observation that the equivalent weight of strontia was almost exactly the arithmetic mean of those for lime and baria.²⁰ By 1829, Döbereiner had extended his initial observation by finding similar trends in certain properties of selected groups of elements.²¹ For example, lithium, sodium, and potassium were well known to have very similar chemical properties, and Döbereiner pointed out the fact that the average of the

Figure 4. Gmelin's "Körpernetze" from his *Handbuch der theoretischen Chemie* (1843).

equivalent weights of lithium and potassium was close to that of sodium.

Döbereiner found other triplets of chemically similar elements whose equivalent weights obeyed the same rule: one was calcium, strontium, and barium, another was sulfur, selenium, and tellurium, and a third was chlorine, bromine, and iodine. Moreover, for some of these triads the gas or solid densities of the elements and "the intensity of chemical affinity" followed a similar pattern. These sets of elements became known as Döbereiner's Triads.

Offprints of Döbereiner's 1829 paper seem not to exist (there is no evidence that any were printed) but one can find copies of the paper in the form of its appearance in the journal *Annalen der Physik und Chemie*.

GMELIN'S NETWORK OF ELEMENTS (1843)

In 1819, the German chemist Leopold Gmelin (1788-1853) published the first edition of his *Handbuch der theoretischen Chemie* [*Handbook of theoretical chemistry*]. The second and third editions had similar titles and arrangements, but the fourth edition was intended to cover all types of chemistry, and Gmelin chose a new title, *Handbuch der Chemie*.²² It is in this fourth edition that Gmelin's remarkable forerunner to the periodic table first appears: his "Körpernetze" or network of elements.

In volume 1 of his *Handbuch*, Gmelin presents a system, based on Döbereiner's triads, which established relationships between 55 chemical elements by arranging triads (or sometimes groups of four, five, or six elements) into an overall V-shape (Fig. 4). Gmelin states that, within the V, the triads are stacked vertically by electronegativity, with the most electronegative triad (F, Cl, Br, I) occupies the upper left of the V, the most electropositive (Li, Na, K) the upper right, and those with intermediate electronegativities (mostly what we now call the transition elements) are placed at the bottom. Within

each triad, the elements are ordered from left to right by increasing atomic weight. Oxygen, nitrogen, and hydrogen are not placed into any of the triads, but instead are given privileged positions above the V.

Gmelin's Körpernetze arranged most of the then-known main group elements in the same fashion (albeit rotated and slanted) as seen in a modern periodic table, despite the handicap of using "pre-Cannizzaro" equivalent weights. Although some of the elements are not arranged "correctly," Gmelin's Körpernetze is still a remarkable achievement.³

Original multivolume sets of the fourth edition of Gmelin's *Handbuch* are fairly readily available for purchase. The eight volumes were issued in nine parts (volume 7 being divided into two parts). Volume 1 is dated 1843 and the following volumes were issued in subsequent years; volume 8 appeared in 1866. Two supplementary volumes were issued in 1868.

NUMERICAL REGULARITIES IN THE ATOMIC WEIGHTS COMMON TO DIFFERENT GROUPS OF ELEMENTS (1850-1860)

In the 20 years after Gmelin published his Körpernetze, several chemists tried to find mathematical regularities among the atomic weights of the elements. Some of these, such as Josiah Parsons Cooke (1827-1894), discussed only regularities that occur within individual groups.²³ The first to propose that there might be regularities that pertain to more than one group of related elements was the German chemist Max von Pettenkofer (1818-1901), in his 1850 article "Ueber die regelmässigen Abstände der Aequivalentzahlen der sogenannten einfachen Radicale [On the regular spacings of the equivalent numbers of the so-called simple radicals]."²⁴

After quoting the passages in Gmelin's *Handbuch* that discuss Döbereiner's triads, Pettenkofer made the observation that the differences in equivalent weights in the alkali metal, alkaline earth, and nitrogen groups (and a few other pairs of elements) are either 8 or a multiple of 8. He then commented, "The recurrence of differences between the cited equivalent numbers of such bodies that belong to a natural group, and which are nearly divisible by 8, is too frequent to be thought to be a mere coincidence in the size of the divisor." Pettenkofer went on to suggest that there the regularities in the equivalent weights of the elements might be analogous to those seen for the organic groups methyl, ethyl, butyryl (i.e., butyl), and amyl, for which the differences in equivalent weights were 14, 28, and 14.

In 1853, in an article entitled "On the Relations between the Atomic Weights of Analogous Elements,"²⁵ the English chemist John H. Gladstone (1827-1902) tried to fit the equivalent weights of several related groups of elements, as given in Gmelin's 1843 network, to formulas of the kind $a + nx$, where n is an integer. Gladstone noted (as Pettenkofer had, but without citing his paper) that similar formulas had recently been found to apply to series of organic compounds such as the methyl-ethyl-amyl series. He went on to comment that there was a regularity that persisted across several groups of elements: the increment x in his formula was 24 for both the Ca-Sr-Ba and S-Se-Te series, and also for the Zn-Cd pair. Gladstone speculated (again, like Pettenkofer) that these and similar regularities were unlikely to be due to chance, and suggested that they might reflect some regular aspect of the inner constitution of the elemental bodies.

In 1858, in his three-part paper "Mémoire sur les équivalents des corps simples [Memoire on the equivalents of simple bodies],"²⁶ the French chemist Jean Baptiste André Dumas (1800-1884) carried out an analysis of the equivalent weights of the elements in terms of algebraic formulas similar to those introduced by Gladstone (although Dumas cited Cooke's later paper²³ of 1854 as the source of the idea). In particular, Dumas fitted the weights to formulas of the type $a + nd + md' + d''$. For some groups, however, fewer than four terms sufficed: the magnesium (i.e., alkaline earth) and oxygen groups, for example, required only the first two terms.

Dumas noted that the elements in the magnesium and oxygen groups could be paired up in such a way (oxygen with magnesium, sulfur with calcium, etc.) that the difference in equivalent weight within each pair was exactly 4; here, Dumas's weights for all these elements are half the modern values. He went on to point out that a similar relationship could be constructed for the halogens and pnictogens,²⁷ except here the difference in equivalent weight between pairs was 5. Dumas illustrated these relationships in a way that, in hindsight, clearly expresses the intergroup relationships of elements in the same period. For example, for the halogen and pnictogen elements, he wrote the atomic weights one below the other in two parallel rows:

Azote 14	Phosphore 31	Arsenic 75	Antimoine 122
Fluor 19	Chlor 35.5	Brome 80	Iode 127

In 1859, the German chemist Adolph Strecker (1822-1871) published a small book entitled *Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente* [*Theories and Experiments on the Determina-*

tion of Atomic Weights of the Elements].²⁸ Strecker's discussion of the numerical relationships among atomic weights occupies the last 10 pages of his book. Much of this section consists of a critical analysis of Dumas's 1857 paper on this topic. But on page 145 Strecker wrote, "If one doubles the atomic weight of the elements in the [carbon group], then the differences of each pair of atomic weights are all $22n$ except between carbon and silicon, where it is 16, i.e., approximately the same number that also is seen for nitrogen, fluorine, lithium and oxygen (if one doubles its atomic weight)." Strecker's statement is the first in the chemical literature that suggests the possibility of modifying the then-current atomic weights so as to create more regular numerical interrelationships with elements from other groups. This idea was to lie fallow until Mendeleev resurrected it with great effect, most notably in 1870, when he multiplied cerium's atomic weight of 92 by 1.5 so as to place it in its proper location between barium and tantalum.

Mendeleev, who had brought Strecker's book with him when he returned from his study abroad in 1859-1861, credits the book with stimulating his interest in atomic weight relationships, an interest that led to his creation of his Periodic System. Years later, Mendeleev wrote, "A. Strecker, in his work *Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente* (Braunschweig, 1859), after summarising the data relating to the subject, and pointing out the remarkable series of equivalents $Cr = 26.2$, $Mn = 27.6$, $Fe = 28$, $Ni = 29$, $Co = 30$, $Cu = 31.7$, $Zn = 32.5$ remarks that: 'It is hardly probable that all the above-mentioned relations between the atomic weights (or equivalents) of chemically analogous elements are merely accidental. We must, however, leave to the future the discovery of the law of the relations which appears in these figures.'²⁹ Mendeleev's great achievement was to do exactly that.

Another notable contribution in this area was made by the American chemist Mathew Carey Lea (1823-1897). In his 1860 paper "On Numerical Relations Existing between the Equivalent Numbers of Elementary Bodies,"³⁰ (Fig. 5), Lea makes several remarkable observations: (1) the equivalent weights of elements with similar chemical properties often differ by 44 or 45; Lea, however, fancifully finds additional pairs of elements related in this way by extending the algebra to negative equivalent weights, (2) the phenomenon of isomorphism is used to correct the equivalent weights of some elements, such as doubling copper's atomic weight to 63.4 (the modern value), thus foreshadowing Mendeleev, (3) the numerical regularities of equivalent weights are used to make some of the first predictions of the existence of undiscovered elements; Lea predicts that an element of equivalent

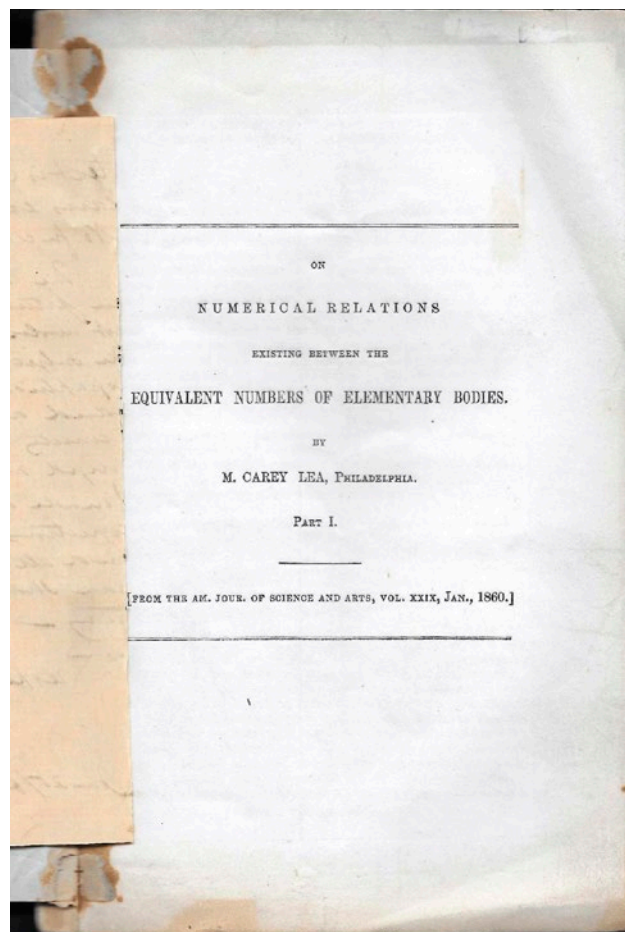


Figure 5. One of two known copies of the offprint of Carey Lea's 1860 paper "On Numerical Relations Existing between the Equivalent Numbers of Elementary Bodies." This particular copy was sent by Lea to the American chemist Franklin Bache (1792-1864), great-grandson of Benjamin Franklin.

weight 164 should be intermediate between antimony and bismuth in the nitrogen group (although incorrect, Mendeleev later made the same prediction), (5) the stoichiometries of recently discovered organometallic compounds, especially those of mercury and phosphorus, are employed to verify valence assignments and atomic weights, much as Edward Frankland (1825-1899) had done a few years earlier, and (6) correlations are sought between the equivalent weights and the atomic volumes of elements in the same group, thus foreshadowing Lothar Meyer's (and Mendeleev's) work ten years later.

The four papers by Pettenkofer, Gladstone, Dumas, and Lea are available to the collector as the journal article, with Pettenkofer's being the hardest to find. Offprints are known only for the Dumas and Lea papers, which can be identified by the renumbering of the pages

beginning with page 1, and by the addition of a separate title page. Both are scarce: slightly more than a dozen copies of the offprint of Dumas's paper are documented, and only two copies of the Lea offprint can be traced. Copies of Strecker's book are also scarce, and many years often separate the appearance of copies for sale.

CANNIZZARO'S PROPOSAL OF A SINGLE SET OF ATOMIC WEIGHTS (1858)

Before about 1860, all those who tried to find more universal relationships among the atomic weights of the elements (as opposed to relationships within individual triads) were handicapped by using equivalent weights that were sometimes true atomic weights and sometimes not; often, the equivalent weights in use in the 1850s and before differed from true atomic weights by a factor of two (and sometimes by other numbers such as 3 or 4 or 3/2). With such sets of equivalent weights, the construction of a periodic system that includes all (or even most) of the elements is essentially impossible.

In 1858, the Italian chemist Stanislao Cannizzaro (1826-1910) wrote two articles that played a decisive role in the formulation of modern atomic-molecular theory and the development of the periodic table. These two papers, which explained how he taught the atomic theory to his students at the University of Genoa, covered both the fundamental concepts of the theory and how it could be used to determine which of the several existing (and incompatible) systems of atomic weights was physically most correct. Cannizzaro's ideas were not new, but instead he emphasized the value of combining the ideas of Amedeo Avogadro (1776-1856) and André-Marie Ampère that equal volumes of gases contain equal numbers of particles, of Pierre Louis Dulong (1785-1838) and Alexis Thérèse Petit (1791-1820) on the constancy of the product of specific heat and equivalent weight (although Cannizzaro does not mention their names), and the definitions of Charles Gerhardt (1816-1856) and Marc Antoine Auguste Gaudin (1804-1880) for the terms "atom" and "molecule."

One of these papers, "Sunto di un Corso di Filosofia Chimica [Sketch of a Course on Chemical Philosophy],"³¹ is well known to chemical historians: it was written in March 1858 and appeared in the May 1858 issue of the journal *Il Nuovo Cimento*. The other paper, "Lezioni sulla teoria atomica fatte nella R. Università di Genova [Lessons on Atomic Theory Given in the Royal University of Genoa],"³² (Fig. 6), is almost unknown, but it is in fact the earlier of the two: it was published in the combined 15 March and 30 March 1858 issue of a Geno-

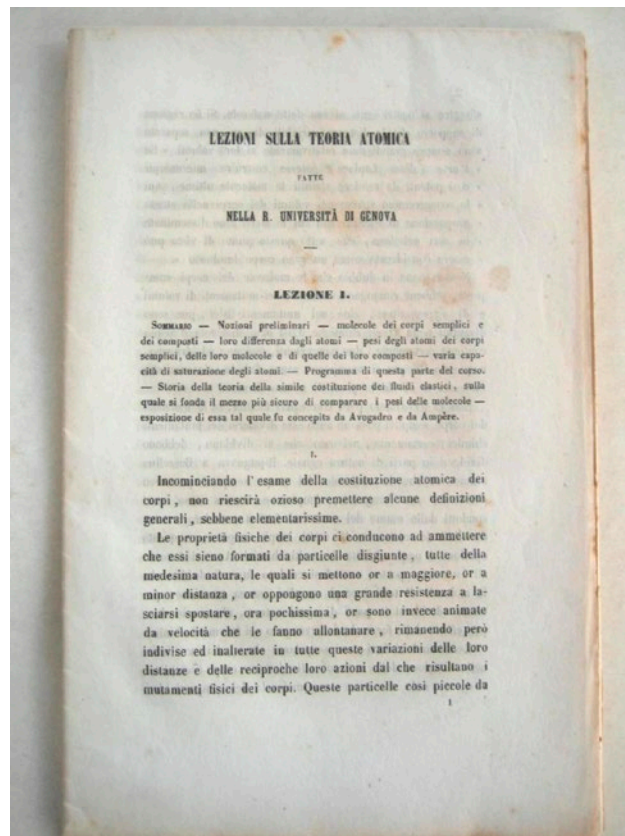


Figure 6. One of five or six known copies of the offprint of Cannizzaro's 1858 paper "Lezioni sulla teoria atomica."

ese periodical, *La Liguria Medica*. As the earlier paper, it therefore is the form in which Cannizzaro first introduced his ideas to the larger scientific community.

Cannizzaro's description of the atomic theory in his *Lezioni* article could be used essentially unchanged in modern textbooks: "Examining the facts, we discover that there is limit to the division of the molecules of every simple body; ... half a hydrogen molecule is the smallest quantity of this body that ever enters whole in the molecules of its compounds. We give to this smallest quantity the name of atom...." In addition to making the distinction between atoms and molecules fully clear, Cannizzaro called attention in this paper to Avogadro's and Ampère's hypothesis and showed how one could use it to determine relative molecular (and atomic) weights from vapor densities.

Cannizzaro's later *Sunto* paper became far better known because copies of it were distributed at the 1860 Karlsruhe Congress, which was attended by many leaders and future leaders in the chemical profession. Among those present were Dmitri Mendeleev and Lothar Meyer, both of whom were impressed by Canniz-

zaro's arguments and became converts to his views; both later cited Cannizzaro's work as a key enabler of their independent development of the periodic table in 1869. Mendeleev wrote, "The decisive moment in the development of my theory of the periodic law was in 1860, at the conference of chemists in Karlsruhe, in which I took part, and at which I heard the ideas of the Italian chemist S. Cannizzaro. I regard him as my immediate predecessor, because it was the atomic weights which he found, which gave me the necessary reference material for my work"³³ and Lothar Meyer commented, "I read [Cannizzaro's paper] again and again and was amazed at the clarity which that short treatise shed on the most important points of contention. Scales fell from my eyes, doubts vanished, and the feeling of the most serene certainty took their place."³⁴

Offprints of Cannizzaro's *Lezioni* paper in *La Liguria Medica* exist but only about five or six are extant; these offprints are distinguishable from the periodical appearance by the repagination and renumbered signatures, by the absence of Cannizzaro's name in the reset title on the first page, and by the statement on the last page that the text was extracted from issues 5 and 6 of *La Liguria Medica*. The journal appearance is almost as scarce.

Cannizzaro's *Sunto* paper appeared in several different forms in the 19th century, including (i) the journal appearance in *Il Nuovo Cimento*; (ii) an offprint from *Il Nuovo Cimento*, which was distributed to the attendees at the Karlsruhe conference in 1860. This 62 page pamphlet was printed in Pisa and also contained the text of Cannizzaro's note on the condensation of vapor, which had appeared in the same issue of *Il Nuovo Cimento*; (iii) an 1880 separate edition, in which the *Sunto* paper was reprinted along with his "Nota sulle condensazioni di vapore," and with his 1858 *Lezione* paper from *La Liguria Medica*. This 80 page pamphlet was printed in Rome, possibly in commemoration of the 20th anniversary of the presentation of Cannizzaro's ideas at the Karlsruhe conference; (iv) the 1896 book *Scritti intorno alla teoria molecolare ed atomica*, which reprints the *Sunto*, the *Nota*, and the *Lezione* papers, along with several other papers by Cannizzaro on related topics. This 387 page text was printed in Palermo to commemorate Cannizzaro's 70th birthday. Two versions of this book are known, one with a frontispiece portrait of Cannizzaro, and one without. The first three of these forms of Cannizzaro's paper are rare: the journal appearance can be found in libraries but is almost unknown in the book market, and fewer than 10 copies of the offprint and the 1880 separate are extant. Only the 1896 book appears regularly for sale.

BÉGUYER DE CHANCOURTOIS'S TELLURIC SCREW (1862-1863)

The *Vis Tellurique*, or Telluric Screw, formulated in 1862 by the French geologist Alexandre-Émile Béguyer de Chancourtois (1820-1886), was an important precursor to the periodic table. In it, Béguyer de Chancourtois positioned the known chemical elements in order of increasing atomic weight on a slanted line wrapped around a cylinder, with 16 mass units per cylinder turn. When he did so, closely related elements lined up vertically. This regularity led him to state that "the properties of the elements are the properties of numbers." He was the first to recognize that the properties of the elements, considered as an entire group and not just within individual triads, are periodic functions of their atomic weights.

Béguyer de Chancourtois's ideas were originally published in several parts³⁵ in the *Comptes Rendus* in 1862 and 1863 but he was frustrated – and the impact of his ideas was blunted – because the journal refused to include a figure showing his helix. As a result, Béguyer de Chancourtois commissioned a combined offprint of his articles under the title *Vis Tellurique. Classement naturel des corps simples ou radicaux obtenu au moyen d'un système de classification hélicoïdal et numérique*. [*The Telluric Screw. Natural Grouping of Simple Bodies or Radicals by means of a Helical and Numeric System of Classification*].³⁶ The combined offprint was distributed with a privately-commissioned printing of the diagram of his helix; it is perhaps not too surprising that the journal did not print the diagram – printed in red, green, and black – because it is 1.45 meters long (Fig. 7).

The offprint of *Vis Tellurique* evidently was issued in at least two editions. The first edition, dating from 1862, was issued in paper wrappers and there is no mention of plates on the title page. A later (second) edition, probably dating from 1863, was issued in printed boards; the subtitle on the title page calls for two plates, the first being described as "Tableau chromolithographié des caractères des corps [chromolithographed table of the characters of bodies]" and the second as "une seconde planche muette, du développement du cylindre disposée pour l'étude et l'extension du système [a second wordless illustration of the development of the cylinder arranged for the study and extension of the system]." The chromolithographed diagram of his telluric helix is always designated as "Première Esquisse" but there are at least three printings, the first dated 7 Avril 1862 and the third dated 16 Mars 1863. I do not know of a copy of the second printing.

As far as I am aware, only four copies of the offprint of *Vis Tellurique* have been offered for sale in the last

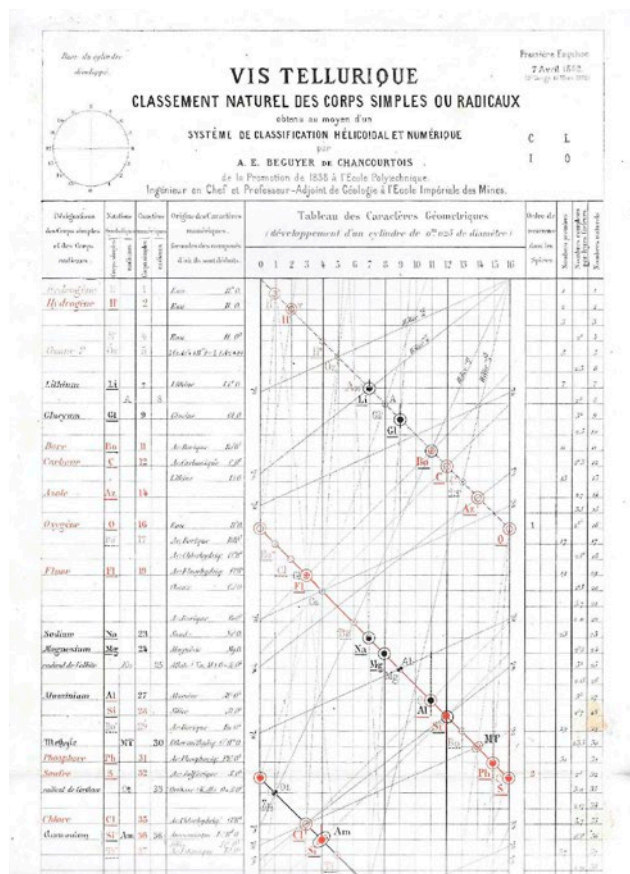


Figure 7. One of about a dozen known copies of the table accompanying the offprint of Béguyer de Chancourtois's 1862 paper *Vis Tellurique*. This figure shows only the upper 25 cm of the 145 cm long chart. This particular copy of the chart is the one that was owned by the Italian chemist Stanislao Cannizzaro

50+ years, and only about 10 copies of the offprint are documented in institutional libraries. The journal issues of the *Comptes Rendus* containing Béguyer de Chancourtois's articles are more readily available, but these lack the all-important diagram.

MEYER'S FIRST PERIODIC TABLE (1864)

A significant advance is seen in the first edition of the book by the German chemist Julius Lothar Meyer (1830-1895), *Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik*. [The Modern Theories of Chemistry and their Meaning for Chemical Statics],³⁷ written beginning in 1862 and published in 1864. Near the end of his book, Meyer included a tabular arrangement of 28 elements, ordered by increasing atomic weight (except for the Te/I inversion). This table

(Fig. 8) depicted the periodic relationships of the elements far more effectively than did Béguyer de Chancourtois's Telluric Screw.

Meyer's table, which arranged the then-known main group elements into six families, contained three important features, although none of these was explicitly discussed in the text: first, the table clearly shows that the valencies of the elements are correlated with atomic weight: the valency decreases from 4 to 3 to 2 to 1 when moving from the carbon group elements (which are at the left of his table) through the pnictogens and chalcogens to the halogens, and then the valency increases from 1 to 2 upon continuing from the alkali metals to the alkaline earths (which are at the right side). Thus, Meyer's table implies that there are regular relationships between different groups of elements. A second important feature that is not explicitly discussed in his accompanying text is that the table includes gaps to denote presumably unknown elements.

Third, the table also contains information about the differences in the atomic weights between elements in the same group but different periods. The differences seen between elements in the first and second row, and between the second and third row, are all about 16, whereas the difference seen for elements in the third and fourth row, and fourth and fifth row, are all between 44 and 49. One of the gaps in the table is below silicon (atomic weight of 28.5) and above tin (117.6), corresponding to the then-unknown element germanium. Meyer's table implies (but does not state) that the atomic weight of this missing element should be about 44.55 larger than that of silicon, and about 44.55 smaller than that of tin.

In addition to the table of main group elements, Meyer presented two additional tables on the following page, the first showing intergroup relationships between six "early" transition metals, and the second showing intergroup relationships among sixteen "late" transition metals (speaking anachronistically). As for the main

	4 werthig	3 werthig	2 werthig	1 werthig	1 werthig	2 werthig
Differenz =	—	—	—	—	Li = 7,03 (Ba = 9,3?)	—
	—	—	—	—	16,02	(14,7)
Differenz =	C = 12,0	N = 14,04	O = 16,00	Fl = 19,0	Na = 23,05	Mg = 24,0
	16,5	16,96	16,07	16,46	16,08	16,0
Differenz =	Si = 28,5	P = 31,0	S = 32,07	Cl = 35,46	K = 39,13	Ca = 40,0
	$\frac{89,1}{2} = 44,55$	44,0	46,7	44,51	46,3	47,6
	—	As = 75,0	Se = 78,8	Br = 79,37	Rb = 85,4	Sr = 87,6
Differenz =	$\frac{89,1}{2} = 44,55$	45,61	49,5	46,8	47,6	49,5
	Sn = 117,6	Sb = 120,6	Te = 128,3	J = 126,8	Cs = 132,0	Ba = 137,1
Differenz =	89,4 = 2,44,7	87,4 = 2,43,7	—	—	(71 = 2,55,5)	—
	Pb = 207,0	Bi = 208,0	—	—	(TI = 204,7)	—

Figure 8. Meyer's periodic table from his 1864 book *Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik*.

group elements, the tables illustrate trends in the valencies (oxidation states) across the groups. Meyer's transition metal triads are somewhat jumbled with respect to the modern placings, but he accurately put Zn, Cd, and Hg into one triad, and Cu, Ag, and Au into another, thus becoming the first to incorporate these triads into a general classification scheme of the elements.

Meyer's book was issued in a very small edition and, as a result, it has long been a rarity in the rare book market. Many well-known private collections of science or chemistry books did not include a copy. My investigations suggest that fewer than a half dozen copies have been sold at auction or by rare book dealers in the last 70 years.

NEWLANDS'S LAW OF OCTAVES (1864-1866)

In July 1864 the chemist John Alexander Reina Newlands (1837-1898), born in London but the son of a Scottish father and an Italian mother, devised a table of 37 of the then-known elements, arranged (mostly) by increasing atomic weight and grouped into ten families. This paper, "Relations between Equivalents," was one of a series of papers on his ideas about the relationships of the chemical elements that Newlands submitted to the journal *Chemical News*.³⁸

In Newland's 1864 table, the main group elements are arranged exactly as in the modern table except that he is uncertain of the place of lithium, and (not too surprisingly given the stabilities of their lower oxidation states) thallium and lead are placed in the alkali metal and alkaline earth groups, respectively. Eight transition elements are included in the table, and several of them are not placed as one would today: osmium is in the oxygen group, gold is in the boron group, zinc and cadmium are grouped with magnesium, and Mo-V-W and Pd-Pt are placed in their own groups.

Newlands's 1864 table leaves gaps in several places, such as those later to be occupied by gallium and germanium. Although he does not discuss these gaps explicitly, he states "So frequently are relations to be met with among the equivalents of allied elements, that we may almost predict that the next equivalent determined, that of indium, for instance [which had been recently discovered], will be found to bear a simple relation to those of the group to which it will be assigned."

In 1865, Newlands published a follow-up paper, "On the Law of Octaves," and in 1866 he gave a talk at a meeting of the Chemical Society that was also abstracted in *Chemical News*.³⁸ In the 1865 paper, he wrote "If the elements are arranged in the order of their equivalents,

with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear in the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves of music.... This peculiar relationship I propose to provisionally call "The Law of Octaves." Here, "the numbers of the analogous elements" are not atomic weights but rather the ordinal number that the element has in his sequence, i.e., akin to (but not) an atomic number.

In his effort to find more regularity in the properties and interrelationships of the elements than he had been able to find in 1864, Newlands forced the elements into seven families, eliminated the gaps from his previous table, and sometimes placed two elements in a single place; the net result is a distinct backward step. In the discussion after Newlands's 1866 talk, John H. Gladstone – whose own contributions to this area are mentioned above – objected to the new table (quite appropriately, as later events showed) because it assumed that no elements remained to be discovered.

Offprints of articles from *Chemical News* from this period do exist, but are unknown for Newland's papers and it is probable that they were never printed. Newlands's original papers in *Chemical News* are readily available as the bound volumes for those years, however, often as library discards. In 1884, fifteen years after Mendeleev announced his Periodic System, Newlands issued a collected reprinting of his articles from the *Chemical News* as the book *On the Discovery of the Periodic Law, and on Relations among the Atomic Weights*.³⁹ Normally, presentation copies of books, i.e., those bearing a signed inscription from the author, are prized because so few exist, but Newlands sent signed copies to a very large number of chemists and institutions. Today, signed copies are frequently seen on the rare book market; unsigned copies are actually not as common.

ODLING'S TABLE OF THE ELEMENTS (1864)

In October 1864, the English chemist William Odling (1829-1921) published a remarkable paper "On the Proportional Numbers of the Elements,"⁴⁰ which contained an important precursor to the periodic table. In this paper, Odling succeeded in arranging 57 elements into a table that looks very much like Mendeleev's first periodic table of 1869 (Fig. 9). Odling stated in his article, "Upon arranging the atomic weights or

				Ro 104	Pt 197
				Ru 104	Ir 197
				Pt 106.5	Os 199
				Ag 108	Au 196.5
H 1	"	"	Zn 65	Cd 112	Hg 200
"	"	"	"	"	Tl 203
L 7	"	"	"	"	Pb 207
G 9	"	"	"	U 120	"
B 11	Al 27.5	"	"	Sn 118	"
O 12	Si 28	"	"	Sb 122	Bi 210
N 14	P 31	As 75	"	Te 129	"
O 16	S 32	Se 79.5	"	I 127	"
F 19	Cl 35.5	Br 80	"	Cs 133	"
Na 23	K 39	Rb 85	"	Ba 137	"
Mg 24	Ca 40	Sr 87.5	"	Ta 188	Th 231.5
	Ti 50	Zr 89.5	"	"	"
	"	Ce 92	"	"	"
	Cr 52.5	Mo 96	"	V 137	"
	Mn 55	"	"	W 184	"
	Fe 56	"	"	"	"
	Co 59	"	"	"	"
	Ni 59	"	"	"	"
	Cu 63.5	"	"	"	"

Figure 9. Odling's periodic table from his 1864 article "On the Proportional Numbers of the Elements."

proportional numbers of the sixty or so recognized elements in order of their several magnitudes, we observe a marked continuity in the resulting arithmetical series.... With what ease this purely arithmetical seriation may be made to accord with a horizontal arrangement of the elements according to their usually received groupings is shown in the following table, in the first three columns of which the numerical sequence is perfect, while in the other two the irregularities are but few and trivial."

Odling's table places the main group elements in the center, and the transition elements above and below them. Odling, like Meyer and Newlands, independently introduced the inversion of the elements tellurium (129) and iodine (127) in order to associate these elements with their chemical relatives. The main group elements are arranged in groups that correspond exactly to the modern groups of elements; the relationships among the transition elements were more difficult to untangle, as they were to be even for Mendeleev.

Odling noted that many pairs of chemically related elements have atomic weight differences that lie between 84.5 and 97 and that, of these pairs, about half are the first and third members of known triads. He added that, "the discovery of intermediate elements in the case of

some or all of the other pairs is not altogether improbable." It cannot be said that these predictions are based on a periodic law; instead, they are predictions based on individual incomplete triads. Most of these predictions, however, didn't pan out because most of the pairs Odling cited had atomic weight differences that (as we now know) are affected by the interposition of the then-unrecognized lanthanide series of elements.

Odling incorporated a modified version of his table in the second (1865) edition of his book, *A Course of Practical Chemistry Arranged for the Use of Medical Students. A Course of Practical Chemistry Arranged for the Use of Medical Students*.⁴¹ Starting on page 226 of that book, after the end of the text, are a series of appended tables. In the first of these, entitled "Atomic Weights and Symbols," 45 elements are arranged much as they are in the modern periodic table, with gaps for nine elements indicated by dashes. Three of the gaps stem from not placing copper, silver, and gold into a triad, and another from not placing chromium, molybdenum, and tungsten together; it is interesting to note that Odling had correctly placed silver and gold together, and chromium and molybdenum together, in his 1864 table. The remaining four gaps correspond to elements that had not yet been discovered: gallium, germanium, technetium, and indium. Unfortunately, Odling nowhere discusses this table in the text, nor does he comment on the gaps.

Mendeleev's first paper on his Periodic System⁴² included a footnote stating that, after his paper had been submitted, he had been informed that a very similar table of elements had appeared in Odling's *Practical Chemistry*. Mendeleev emphasized that he had not been aware of Odling's table before this time.

No offprints of Odling's 1864 paper are recorded, but it is available as the bound journal volume. The 1865 edition of Odling's *Practical Chemistry* is remarkably scarce and rarely appears for sale; the other editions (1854, 1869, 1876) seem to be more common but none contains Odling's table.

HINRICHS'S PROGRAM OF ATOMECHANICS (1867)

The last of the contributions to the development of the periodic table that we will discuss in the present article were made by the chemist Gustavus Detlef Hinrichs (1836-1923); Hinrichs had been born in Holstein, then part of Denmark but now part of Germany, but had immigrated to the United States in 1861. In 1867, he privately published a lithographed reproduction of a 44 page hand-written treatise, entitled

Programme der Atomechanik, oder die Chemie eine Mechanik der Panatome [Program of Atom mechanics, or Chemistry a Mechanics of Panatoms].⁴³ He also wrote an abstract in French and a 4 page abstract in English, the latter submitted in August 1867 to the *American Journal of Mining*.⁴⁴

Hinrichs, like many of those mentioned above, was passionately devoted to the challenge of finding deep meaning in the atomic weights of the elements (and other phenomena, such as the orbital radii of the moons of the outer planets and the wavelengths of the dark lines in the solar spectrum). He proposed that there was a unit of matter, which he called a panatom, which had an atomic weight equal to half of that of hydrogen. He further proposed that there were two kinds of atoms, which he called trigonoids and tetragonids; the former had inner structures consisting of stacks of trigonal/hexagonal arrays of panatoms, whereas the latter had inner structures consisting of stacks of square arrays of panatoms. His attempts to shoehorn the elements into these two classes are replete with ad hoc assumptions to account for the deviations of the atomic weights from the numbers that one would expect from such stacks.

After presenting this proposal for atomic structure in his *Programme der Atomechanik*, Hinrichs then proposed a spiral classification scheme for the elements in which those with larger atomic weights appear at larger distances from the center of the spiral (Fig. 10). His scheme captures some of the intergroup relationships

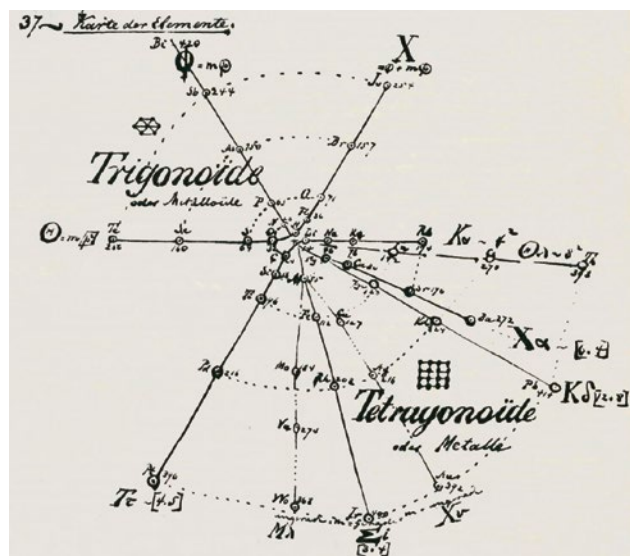


Figure 10. Hinrichs's spiral periodic table from his 1867 book *Programme der Atomechanik*. Image reproduced with permission of the University of Dresden.

that are present in the modern periodic table, but there are many oddities. Most notably, the nitrogen group elements are placed between the chalcogen and halogen groups. The transition elements are again mostly jumbled, although Hinrichs (like Lothar Meyer before him) grouped copper, silver, and gold together.

Two years later, Hinrichs published a revision of his classification system in two papers, one presented in August 1869 to the 18th annual meeting of the American Association for the Advancement of Science, "On the Classification and the Atomic Weights of the so-called Chemical Elements, with reference to Stas' Determinations,"⁴⁵ and the other the same summer to the journal *The Pharmacist*, "Natural Classification of the Elements."⁴⁶ In these two papers, the nitrogen group is now in its modern place relative to (i.e., between) the oxygen and chlorine groups. But other oddities are introduced; for example, the transition elements are listed in reverse order of their atomic weights. Hinrichs's tables of 1869 contain numerous gaps, but he gives no indication that the gaps are significant.

Hinrichs's 1869 table is tabular instead of spiral: the elements within a period being listed in a vertical column, and elements within a group being arranged in rows from left to right. Of all the early attempts to arrange the elements in tabular form, only Odling's table of 1864 and Mendeleev's first table of 1869 are arranged in this way.

Hinrichs clearly recognized the periodic interrelationships that are brought out by his tables: "[I]n this table the elements of like properties, or their compounds of like properties, form groups bounded by *simple lines*. Thus a line drawn through C, As, Te, separates the elements having metallic lustre from those not having such lustre. The gaseous elements form a small group by themselves,... so also the ... *heavy metals* (specific gravity above five)... Of great practical importance are the lines expressing certain properties of definite compounds [such as] solubilities ... reactions in the wet way [and] blowpipe reactions...."

To my knowledge, no copies of Hinrichs's 1867 *Programme der Atomechanik* have been available for purchase on the rare book market in the last 50 years. The American Academy for the Advancement of Science printed a proceedings volume that contained the text of all the papers (including Hinrichs's) presented at their 1869 meeting; copies of this volume can occasionally be found for sale. Hinrichs also reprinted this paper (using the same setting of type) as paper no. 4 of his *Contributions to Molecular Science, or Atomechanics*.⁴⁷ I have not seen an original copy of this reprint available for sale in recent decades.

CONCLUDING REMARKS

With the contributions of Hinrichs, the stage was set for the entrance of Mendeleev into the story in 1869: in that year, Mendeleev circulated a privately-printed periodic table and also published it in both a journal article⁴² and a textbook, *Osnovy Khimii*.⁴⁸ It is important to point out, however, that the discussion above lists only some of the principal documents that led more or less directly to the concept of the periodic law. Many other contributions, which either were important but peripheral or were later recognized as blind alleys, have been omitted for the sake of brevity. But this brevity necessarily paints a distorted picture of how this important and fascinating area of science actually developed.

Many of the books and papers mentioned above are quite rare: for some, fewer than a dozen copies exist, but others are more common and appear regularly for sale at auction or by rare book dealers. Acquiring all of these foundational documents in a collection devoted to the history of the periodic table, in the original editions, would be a challenging but enjoyable pursuit. Holding these documents in one's hands conveys a real sense of connection with the great scientists of the past. This sense is especially keen if the pamphlet or book bears a handwritten inscription from the author, such as the copy of Dalton's *New System* shown in Figure 3. Such special copies, known as presentation copies among collectors, are very hard to find and are considerably more interesting (and valuable) than ordinary copies. In addition, the documents often contain the signatures of one or more former owners. Although sometimes the previous owners are well known scientists, more often they are not. Tracking down their identities can be a challenging puzzle that calls upon skills and methods similar to those employed when tracing family genealogies.

As is true of all collecting hobbies, the hunt for and capture of suitable items to acquire is an endeavor of continual pleasure. The process affords opportunities to meet dealers and other collectors who share similar interests, and can result in long-lasting friendships. Rare book dealers are often scholars themselves who not infrequently add to our understanding of history. Without their unflagging passion to locate great books and find good homes for them, both private and public libraries would be much the poorer.

But even if forming a collection is not one's primary goal, these documents remain of great interest, and they can be viewed in person at major institutional libraries.⁴⁹ By consulting them in their original forms, much can be learned about key parts of the path that led to the crea-

tion of the periodic law and its iconic table, one of the triumphs of modern science.

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- directly, the offprints necessarily went through the author's hands, they often bear presentation inscriptions, and they sometimes were printed days to years before the journal issue appeared, so that the offprint was often the form in which a scientific result was first made available to the world. Owing to their direct physical connection with the author and their scarcity, offprints of significant articles (such as those discussed here) can be quite valuable.
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