Dmitri Mendeleev and the Periodic System: Philosophy, Periodicity, and Predictions

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Abstract

One of the projects undertaken by chemists during the first half of the nineteenth century was organizing the elements in a meaningful way. By the time of the Karlsruhe Conference in 1860, it was clear that atomic weight was likely the key to creating an organizational scheme that could encompass most, if not all, of the elements rather than small groupings. When Dmitri Mendeleev developed his periodic law in 1869, others had already created systems in which the elements were organized by atomic weight, in which it was postulated that the atomic weights of some elements should be adjusted, and in which gaps were left for elements that had not yet been discovered. These are also hallmarks of Mendeleev's system, yet it is his system which gained wide attention and acceptance. This paper looks at Mendeleev's system in relation to those of his contemporaries. Three areas that Mendeleev emphasized as important in his writings will be explored in greater depth: his philosophical understanding of elements, which assisted in the development of the periodic law; his detailed predictions for elements not yet discovered, which showcased the utility of the periodic system; and his stress on the finiteness of periods, which influenced what he saw as the best forms of the periodic table.

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2.1 Introduction

In a lecture on the history of chemistry, German chemist Alfred Ladenburg informed his audience that natural laws "do not originate suddenly in the head of a single individual" [1]. Rather, over time and through the work of many, the facts are determined and the fundamental ideas mature. It is then that someone, or several someones, announce the law. The history of the periodic law follows this pattern. Chemists spent much of the nineteenth century creating different ways to organize and classify the elements. None of these schemes was entirely satisfactory, however, as many failed to encompass all of the elements and most lacked a single fundamental property upon which a system could be based. When Dmitri Mendeleev developed his periodic law in 1869, he built upon what he referred to as "the stock of generalisations and established facts which had accumulated by the end of the decade 1860–1870" [2].

This paper begins with an overview of the organization and classification of the elements before Mendeleev and then considers three areas Mendeleev emphasized in his writings which shaped his understanding of the periodic system. His philosophical understanding of elements assisted in the development of the periodic law. His detailed predictions for elements not yet discovered and reasons for changing the atomic weights of some elements showcased the utility of the periodic system. His stress on the finiteness of periods influenced what he saw as the best forms of the periodic table.

2.2 Classification Before Mendeleev

Over the course of the first half of the nineteenth century, chemists searched for meaningful ways to organize and classify the chemical elements. In his *A New System of Chemical Philosophy*, John Dalton had tied atomic weight to the identity of an element [3]. While not all of Dalton's chemical atomic theory was accepted, atomic weight quickly became the defining characteristic of an element and the determination of atomic weights became an important field of research. It was noticed early on that there was an arithmetic relationship between small groupings of elements. These so-called triads were composed of three elements with similar chemical properties in which the atomic weight of the center element was the mean of the weights of the other two elements.[1] For example, in the grouping of calcium, strontium, and barium, the atomic weight of strontium was the mean of that of calcium and barium. These triads, however, were just that, groups of three. There was no obvious way to connect all of the elements in a numerical relationship. There were few attempts to do so, in part because there was a lack of accurate atomic weights. Chemists knew that atomic weights were highly uncertain. Multiple bases for calculating weight and multiple understandings of the term atomic

[1]For more on triads, see Chapter 3 of this volume.

weight made a single system based on that criterion difficult. A better method for the determination of atomic weight became well-known in 1860, but until then other means of organization needed to be used.

2.2.1 Before 1860

One of the most commonly used methods of classifying the elements was to divide them into two groups, metals and metalloids (or non-metals). This was a seemingly straightforward system that nonetheless caused confusion. As Leopold Gmelin wrote in his noted handbook, “No exact line of demarcation can be drawn between metals and metalloids” [4]. For example, some chemists placed iodine with the metals as it had a visible metallic luster while others considered it to be a metalloid based on other characteristics. It was a system based on only one characteristic but one which was not always the most important characteristic of an element and one which was open to interpretation. Other methods for classifying and organizing the elements were sought.

2.2.1.1 Gmelin

Leopold Gmelin had been studying the numerical relationships between the elements since at least 1827. His arrangement displays triads, the word he used in place of Döbereiner’s triplets [5]. In 1843, Gmelin published a system of the elements in the fourth edition of his *Handbook of Chemistry*. Gmelin divided the known elements into metals and metalloids. But, as noted, he was clear that it was not an easy division to make. Based on triads, he then arranged the elements in groups according to their chemical and physical properties. This was shown in a table with a vee shape (Fig. 2.1). It was an “imperfect attempt” to arrange the elements and he noted it would be better shown in three dimensions [4]. Across the top of the vee were oxygen, hydrogen, and nitrogen, as none had a known analogous element. The electro-negative elements were placed on the left and the electro-positive elements on the right [6].

2.2.1.2 Gladstone

In 1853, in an ordering that was unusual at the time, British chemist John Hall Gladstone placed all of the elements in order according to their atomic weights.[2] However, he did not see any obvious relationships. According to Francis Preston Venable, the American chemist who wrote the first history of the periodic law, this was because “the numbers used by Gladstone are too faulty to show any noteworthy regularity” [7]. Gladstone then grouped the elements as Gmelin had done but replaced the symbols of the elements with their atomic weights. He discerned some numerical relationships in doing this, but they were largely triads. Why this was the case, he did not know, but he was sure that these numerical relationships were not

[2]Venable states Gladstone was the first to do so, but this is incorrect. Marc Antoine Gaudin did so in 1833, and before that Dalton published several partial lists organized in this way.

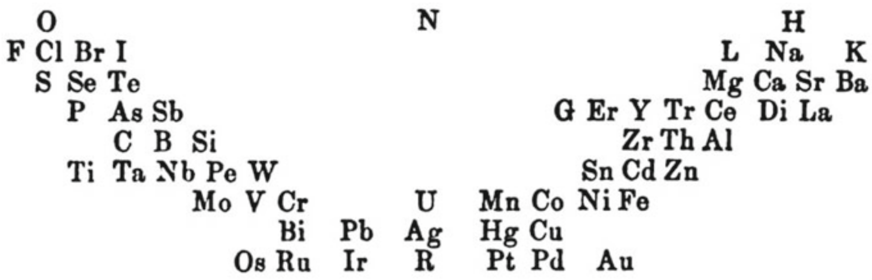

Fig. 2.1 Gmelin's vee shape classification. Reproduced from Gmelin (1844) [4]

mere chance. Further research was required, but he was hopeful an answer would soon be found: "We can scarcely imagine that the intimate constitution of these related elementary bodies will long remain an unfruitful field of investigation" [8].

2.2.1.3 Cooke[3]

Josiah Parsons Cooke, Jr., who taught chemistry at Harvard College, found the use of only one characteristic as the basis of a classification system to be ridiculous. He wrote in 1855 [9]:

> For a zoologist to separate the ostrich from the class of birds because it cannot fly, would not be more absurd, than it is for a chemist to separate two essentially allied elements, because one has a metallic lustre and the other has not.

Rather a "correct" classification system should be based upon a "fundamental property common to all the elements, the law of whose variation is known." However, it was not clear what that common fundamental property was. Such a system also needed to encompass all of the elements, not just groups of triads. Cooke created a classification in which the elements were placed into six series, each containing elements that formed similar compounds and produced similar reactions, had the same crystalline forms, and whose properties varied in a regular manner [10].

2.2.2 The 1860s

A seminal event in the history of chemistry took place in 1860: an international congress of chemists was held in Karlsruhe to discuss important aspects of chemistry.[4] Among the matters discussed were the definitions of the terms atom, molecule, and equivalent; a uniform chemical notation and nomenclature; and the

[3]For more on Cooke, see Chapter 4 of this volume.
[4]The Karlsruhe Congress was international in that chemists came from 11 European countries, with a lone representative from Mexico. No chemists from the United States or Asia were present.

question of equivalent weights and formulae [11, 12]. As Venable had noted about the atomic weights used by Gladstone, there were many ways to determine the atomic weights of the elements but the conversion of chemical analyses to atomic weight remained uncertain. Perhaps the most important thing to happen at the Karlsruhe Congress occurred at the end, when Italian chemist Angelo Pavesi distributed copies of an article written by his colleague Stanislao Cannizzaro. In it, Cannizzaro described a method for determining atomic weight using the hypothesis of Amedeo Avogadro and André-Marie Ampère [13]. Julius Lothar Meyer later recalled that after reading it, “It was as though the scales fell from my eyes, doubt vanished, and was replaced by a feeling of peaceful certainty” [14].

2.2.2.1 Chancourtois[5]

The French geologist Alexandre-Émile Béguyer de Chancourtois presented a series of papers before the Académie des Sciences in 1862. He described the natural classification of the elements he had developed. Although he had prepared a full diagram of his vis tellurique, it was not published in the *Comptes Rendus* but rather in a self-published pamphlet [15]. Chancourtois’s system was designed to be shown on a three-dimensional helix. The elements were placed on the helix in order of their atomic weight. His key insight was that, “The properties of the bodies are the properties of the number” [16]. In other words, the properties of the elements were tied to their atomic weights. Despite the importance of this insight, Chancourtois’s work received little attention until after Mendeleev’s periodic law had gained acceptance [17].

2.2.2.2 Hinrichs[6]

Danish-American Gustavus Detlef Hinrichs first hinted at his classification in an 1866 paper, stating that a series of papers was forthcoming that would show “the properties of the elements as functions of their atomic weights” [18]. These papers were not published and Hinrichs self-published his classification system in 1867 [19]. In his arrangement, the elements were placed in a spiral in order of atomic weight. The lightest elements were closest to the center of the spiral while the heaviest were furthest away. This spiral arrangement was not easy to read or to print and Hinrichs later produced a tabular form which he used in his textbooks and other publications [20].

2.2.2.3 Odling[7]

English chemist William Odling made several attempts to classify the elements. In his 1857 attempt, he noted, much like Cooke, that although it was an acknowledged fact that “the groupings of the elements are as real and certain as the natural families of plants and animals,” in the usual systems “bodies manifesting the strongest analogies are widely separated from one another.” Starting with triads, he arranged

[5] For more on Chancourtois, see Chapter 5 of this volume.
[6] For more on Hinrichs, see Chapter 7 of this volume.
[7] For more on Odling and Newlands, see Chapter 6 of this volume.

the elements into 13 groups that shared important properties, emphasizing the use of “fundamental” characteristics rather than “superficial” ones [21]. In his 1864 work, Odling organized the elements into a table. He left blank spaces as he felt that the discovery of new elements “is not by any means improbable.” He also noted that the numerical relations between the elements must “depend upon some hitherto unrecognized general law” [22]. Odling’s table appeared as an appendix in the 1865 edition of his textbook, *A Course of Practical Chemistry Arranged for Use of Medical Students* [23] and its French translation [24].

2.2.2.4 Newlands

John Alexander Reina Newlands, an English chemist, published several short works in the weekly magazine *Chemical News* during the 1860s as he developed what he referred to as the Law of Octaves [25]. Newlands arranged the elements by atomic weight and discerned that “the numbers of analogous elements generally differ by 7 or by some multiple of seven,” meaning that the same characteristics reappeared every eight elements. He arranged the elements in the order of increasing atomic weight in a table of eight columns and seven rows [26]. Given that a number of new elements had recently been discovered, Gladstone wondered if “the finding of one more would throw out the whole system” but Newlands believed that the finding of new elements or the revision of atomic weights would not “upset, for any length of time, the existence of a simple relation among the elements, when arranged in the order of their atomic weights” [27, 28]. For his Law of Octaves, Newlands was awarded the Royal Society’s Davy Medal in 1887 [29].

2.2.2.5 Meyer[8]

Although Mendeleev is often credited as the sole discoverer of the periodic law, German chemist Julius Lothar Meyer has a good claim for the title: he was, with Mendeleev, awarded the Royal Society’s Davy Medal in 1882 [30]. After attending the Karlsruhe Congress and reading Cannizzaro’s article, Lothar Meyer began work on a chemistry textbook that would become a classic text, *Die modernen Theorien der Chemie* [31, 32]. As Meyer revised his textbook, he also continued to develop his classification of the elements. The first edition of 1864 contained a table with only 28 of the known elements [33]. By 1868, the table contained 52 elements, the vast majority, arranged by atomic weight and organized in 15 families [34] —but this table was not published until 1895.

In response to Mendeleev’s first announcement of the periodic law, Meyer published another table that he described as being “essentially identical with that given by Mendeleev.” This table included 56 elements in nine columns. There were gaps that he felt would be filled either by already known elements, once their atomic weights had been more accurately determined, or by yet unknown elements. He also included a second figure, one that would become very well-known in the following decades. The atomic volume curve illustrated the variation of atomic volume of solid elements when plotted against atomic weight. It clearly showed, he

[8]For more on Meyer, see Chapters 8 and 9 of this volume.

wrote, "that the atomic volume of the elements, like their chemical properties, is a periodic function of their atomic weight." Although he believed the curve showed there were errors in the accepted atomic weights of several elements, he stated that it would be "premature" to make changes [35].

2.3 Mendeleev's Periodic Law

Much has been written about Mendeleev's discovery of the periodic law so only a very brief overview will be given here [36–39]. Just as Meyer was working on a classification system for the elements while writing and revising his textbook *Modernen Theorien*, Mendeleev was working on a textbook of inorganic chemistry, *Principles of Chemistry*, having already written an organic chemistry text. He was seeking "some system of simple substances in order to be guided in their classification—not by arbitrary or subjective reasons, but by some exact, definite principle" [40]. Mendeleev began arranging the elements by their atomic weights and realized, much as Newlands had, that properties of the elements recurred on a regular basis. The periodic law, as he stated it in his important paper of 1871, was thus: "The properties of the elements (and of the simple and compound substances which they form) show a periodic dependence on their atomic weights" [41].

2.3.1 Mendeleev's Writings on the Periodic Law

Mendeleev wrote many papers relating to the periodic system [42]. The very first paper published in 1869 served to announce and explain his discovery [43]. The seminal 1871 paper, originally published in German, based on earlier Russian papers, and later translated into French and English,[9] provided an in-depth look at the periodic law, how it was applied to create a system of the elements, and how it could be used to discover new elements, correct atomic weights, and otherwise complete our knowledge of the elements [44]. In 1889, Mendeleev was asked by the Chemical Society of London to deliver the Faraday Lecture and he used the opportunity to reflect on the discovery and use of the periodic law and to comment on more recent trends in chemistry [2]. Each edition of his textbook, *The Principles of Chemistry*, also included thoughts about the periodic system.

These writings emphasize three areas which were important to Mendeleev's conception of the periodic system: his philosophical understanding of elements, which assisted in the development of the periodic law; his detailed predictions for elements not yet discovered and changes in atomic weights of known elements,

[9]The French translation was made eight years after the original German publication and Mendeleev included a brief letter in which he provided some new thoughts on the periodic law. The English translation, serialized in the weekly *Chemical News*, was hastily done; see Jensen [41] for a more accurate version.

which showcased the utility of the periodic system; and his stress on the finiteness of periods, which influenced what he saw as the best forms of the periodic table.

2.4 Philosophical Conception of the Chemical Element

In 1810, Dalton defined the term element in this way [45]:

> By elementary principles, or simple bodies, we mean such as have not been decomposed, but are found to enter into combination with other bodies. We do not know that any one of the bodies denominated elementary, is absolutely indecomposable; but it ought to be called simple, till it can be analyzed.

For most of the nineteenth century, the terms “simple body” and “simple substance” were generally used interchangeably with the term “element.” Mendeleev, however, saw a distinction between elements and simple substances [46]. In a lecture given at St. Petersburg University in 1867, he gave a definition for simple substances which is almost identical with Dalton’s definition of elements. A simple body, Mendeleev said, is a substance “which taken individually, cannot be altered chemically by any means produced up until now or be formed through the transformation of any other kinds of bodies.”

Mendeleev described elements as something else altogether—an abstract concept. An element was “the material that is contained in a simple body and that can, without any change in weight, be converted into all the bodies that can be obtained from this simple body” [47]. The frequently given example is that carbon is an element while graphite and diamond are simple bodies. We cannot see the element carbon in the diamond, but it is still present in the simple body that is the diamond.

The clearest statement of this distinction can be found in his first major paper of 1869 [40]:

> everybody understands that in all changes in the properties of simple substances, something remains unchanged and that, in the transformation of the elements into compounds, this material something determines the characteristics common to the compounds formed by a given element. In this regard only a numerical value is known, and this is the atomic weight appropriate to the element.

Continuing with the example of carbon, Mendeleev states that atomic weight does not belong to coal or diamond but to carbon. He thus tied atomic weight to this abstract concept of element.

By 1860, the theories of Charles Frédéric Gerhardt and Stanislao Cannizzaro as well as advances in experimental analysis resulted in increasingly more reliable atomic weights. For this reason, Mendeleev felt confident in basing his classification system for the elements upon atomic weight. It was the fundamental property common to all the elements that Cooke had been looking for and it was the basis for the unrecognized general law that Odling was sure explained the numerical relations between the elements.

Historian Helge Kragh stated that Mendeleev's periodic law "was about both elements and simple substances, but in different ways" [48]. The periodic law was primarily about atomic weight—Mendeleev's elements—as it was the basis for the law. The properties of the elements—Mendeleev's simple substances—showed a periodic dependence on the atomic weight, which was an important aspect of the law.

Mendeleev clearly had a philosophical point of view when it came to the elements. However, unlike previous systems, "the periodic law furnishes facts and emphasizes that philosophical question which highlights the mysterious nature of the elements" [49]. The philosophical question was the nature of the elements. For Mendeleev, the nature of the elements depended on their atomic weight. The periodic law was based "on the solid and wholesome ground of experimental research" whereas other supposedly philosophical ideas about the nature of the elements were "relic[s] of the torments of classical thought," remnants of an ancient time when our ancestors concocted hypotheses to explain the universe [2].

The periodic law had, of course, not yet been proved when he first wrote about it in 1869, but Mendeleev was certain that "new interest will be awakened in the determination of atomic weights, in the discovery of new simple substances, and in the detection of new analogies among the elements" [40]. With this statement, Mendeleev suggested that the periodic system could assist in future research in ways that he explicated in greater detail in his 1871 paper.

2.5 Predictions and Adjustments

Mendeleev discussed the application of the periodic law to the following areas in his 1871 paper: the system of the elements, the determination of atomic weights of insufficiently studied elements, the determination of the properties of presently unknown elements, the correction of the magnitude of atomic weights, and the completion of our knowledge of the forms of chemical combinations [41]. In regard to the periodic system, Mendeleev noted that it held not only "purely pedagogic importance as a means of learning more easily various facts" but also scientific importance as it "paves the way for new methods of investigating the elements." Most famously, Mendeleev left gaps in his periodic tables that he was confident would be filled by as-yet-undiscovered elements. He also corrected the weights of several elements and suggested some others were incorrect. The work of other chemists would prove that Mendeleev was correct: the periodic system was a useful tool for research.

2.5.1 Leaving Gaps and Predicting Characteristics

Mendeleev was far from the first to leave gaps in his table for new elements. Newlands, in his Law of Octaves, had not, although he admitted that new elements would be able to slide into his system. Odling did leave blank spaces in his tables as he felt new elements would be discovered. Meyer also left gaps that, he later explained, would be filled by already known elements after their atomic weights had been more accurately determined or by elements yet unknown. None of them was as bold as Mendeleev who not only left gaps but predicted the atomic weights and chemical and physical properties of the elements that would fill those gaps. As these gaps were filled with newly discovered elements that, more or less, fit Mendeleev's predictions, chemists increasingly began to view the periodic system as a useful tool for both research and pedagogy.[10]

2.5.1.1 Gallium

The French chemist Paul-Émile Lecoq de Boisbaudran announced the discovery of a new element in 1875, which he decided to call gallium in honor of France. After reading of this discovery, Mendeleev composed a note for the *Comptes Rendus* in which he reminded his audience that he had proposed the periodic law in 1869. The note also included a table which had blank spaces, one of which was for an element Mendeleev had called eka-aluminum as it should be analogous to aluminum. The characteristics he had predicted for eka-aluminum were more or less in agreement with those of the newly discovered gallium. He concluded by stating, "If subsequent researches confirm the identity of the properties of gallium with those which I have pointed out as belonging to eka aluminum, the discovery of this element will furnish an interesting example of the utility of the periodic law" [50].

Boisbaudran denied that he was aware of Mendeleev's periodic law or of his predicted element eka-aluminum. He was skeptical that gallium was eka-aluminum and of the utility of Mendeleev's system. He said, "I will even add that this ignorance may perhaps have been advantageous to me, for I should have experienced serious delays" [51]. M. M. Pattison Muir, the British chemist who translated Mendeleev's note on gallium into English, expressed some skepticism himself, believing that further research was required before accepting that eka-aluminum was gallium. However, he declared, "Mendelejeff's hypothesis is at least of much value as a guide to future research" [52].

2.5.1.2 Scandium

Four years after the discovery of gallium, the Swedish chemist Lars Fredrik Nilson discovered a new element among minerals found only in Scandinavia. He called this new element scandium. Nilson was also apparently unaware of Mendeleev's predictions; however, Swedish chemist Per Cleve was aware and he explicitly made the connection in his publication reporting on his research which confirmed the discovery of scandium. He wrote: "The great interest of scandium is that its existence has been predicted. Mendeleef, in his memoir on the law of periodicity, had foreseen the existence of a metal which he named ekabor[on], and whose characteristics agree very fairly with those of scandium" [53].

[10]For more on discoveries of Mendeleev's predicted elements, see Chapter 10 of this volume.

Mendeleev saw that interest in his periodic system had been strengthened and he had a French translation of his 1871 paper sent to the journal *Le Moniteur Scientifique*. It was accompanied by a letter in which he expressed his gratification that his law was under scrutiny and proving itself through experimentation. These recent discoveries were but “the first fruits of the periodic law” and he hoped they would lead to “a new philosophical order, by securing it with pillars strengthened by new experiments, so as to give greater stability to the edifice already begun” [49].

2.5.1.3 Germanium

The discovery of eka-silicon came 15 years after its prediction. In 1886, Clemens Winkler announced the discovery of a new element he called germanium. Initially, he believed it would fit into the periodic system between the elements antimony and bismuth [54]. Further experiments revealed an atomic weight of 72.32 and many of the properties of the new element correlated with those Mendeleev had predicted for eka-silicon [55]. Winkler was not immediately convinced that germanium was eka-silicon but after discussions with Victor von Richter, Lothar Meyer, and Mendeleev, Winkler changed his mind. Germanium fit in the periodic system between gallium, the first of Mendeleev’s predicted elements to be discovered, and arsenic. This discovery served to further strengthen the acceptance of Mendeleev’s periodic law.

2.5.2 Changing Atomic Weights

Mendeleev is renowned for changing the atomic weights of some elements in order to make them better fit into his periodic system. The most well-known of these changes are the pair reversals. Pairs of elements, such as tellurium and iodine, were flipped, giving precedence to their chemical properties rather than to their accepted atomic weights. Odling, Newlands, and Meyer had also flipped tellurium and iodine, but Mendeleev flipped more than one set of elements. Mendeleev is also well-known for doubling the atomic weight of uranium, from the accepted weight of 120 to 240. Perhaps one of Mendeleev’s lesser known adjustments was to the atomic weight of beryllium. In a memoir on beryllium, the American chemist Charles Lathrop Parsons noted that between 1873 and 1885, “a long, earnest and interesting discussion … regarding the valency of beryllium and its place in the periodic system” took place [56]. By the end of this period, many chemists who had remained skeptical about the utility of the periodic system had changed their positions.

The assignment of the atomic weight of beryllium was a test of the accuracy of the periodic system. Chemists believed the atomic weight of beryllium was close to either 9 or 13.5, but there was no consensus. Mendeleev believed that beryllium, or glucinum as it was also called, was divalent and had an atomic weight of approximately 9. Its characteristics made it analogous to magnesium. Odling, Newlands, and Hinrichs had also assigned the atomic weight of 9 to beryllium in their systems. However, others believed that beryllium was trivalent with an atomic weight closer to 13.5, making it analogous to aluminum. In an 1880 paper on their experiments, Swedish chemists Lars Fredrik Nilson and Sven Otto Pettersson announced that their results showed beryllium to have an atomic weight of 13.65. “In consequence of what has been indicated here,” they wrote, “the periodic law in its present condition cannot be said to be quite an adequate expression of our knowledge of the elements.” However, they expected that “the periodic law may be so modified and developed that it can embrace and explain every fact stated by experiment” [57].

The English chemist Thomas Samuel Humpidge, professor of chemistry at the University College of Wales, surveyed the field of beryllium research in an 1880 paper. He preferred to accept fact over theory, writing, “I am not arguing for the rejection of the periodic law, but only wish to show that if facts are discovered which are incompatible with it, it must of necessity receive some modification” [58]. Humpidge obtained a grant from the Royal Society of £50, which went toward materials and apparatus, and began his own experiments.

In his 1883 report, Humpidge described his experimental results which resulted in a specific heat measurement that was “nothing near” what it should be if the atomic weight of beryllium was 9. “The result is unfortunate for the periodic law, and is the first serious rebuff which this useful generalisation of facts has received,” he concluded [59]. Humpidge continued his experiments on the vapor-density of several compounds of beryllium. The results now showed that beryllium was divalent with an atomic weight of 9.1. In his second paper, he declared [55]:

> The long disputed question of the atomic weight of glucinum is thus definitely and finally decided in the favour of that number which satisfies the requirements of the periodic law, and another element is added to the long list of those whose atomic weights have been corrected by this important generalisation.

Over the course of his research, Humpidge changed his opinion on the utility of the periodic system. He wrote, “In all future determinations of the atomic weight of an element, the position which the element should occupy in the periodic arrangement must receive due importance.”

Regarding the controversy over the atomic weight of beryllium, Mendeleev stated that the confirmation of the bivalency of beryllium was “as important in the history of the periodic law as the discovery of scandium.” And, he observed, “It is most remarkable that the victory of the periodic law was won by the researches of the very observers who previously had discovered a number of facts in support of the tri-valency of beryllium” [60].

2.6 The Importance of Periodicity

One important aspect of Mendeleev’s periodic system is the way it is represented graphically. In other words, the periodic table. To date, probably over 1000 different forms of the periodic table have been drawn [61–63]. Mendeleev himself drew more than 60 different tables during his lifetime [64]. Whereas he was bold in his predictions of new elements and in changing the atomic weights of already known elements, Mendeleev was, as historian Bernadette Bensaude-Vincent noted, “more hesitant about the best visualization of the periodic system that he discovered” [65]. He may have been hesitant about what the best form of the periodic table might be but he definitely had opinions about what the best forms were not. Mendeleev frequently noted that the important aspect of the periodic law was just that, periodicity. In *The Principles of Chemistry*, he wrote, “The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.” He further emphasized this point in a footnote about the representation of the periodic law, stating that the law [66]:

> *above all*, depends on there being but few types of chemical compounds, which are arithmetically simple, *repeat themselves*, and offer no uninterrupted transitions, and therefore each period can only contain a definite number of members.

In other words, periods were finite, not continuous, and this fact influenced Mendeleev’s views on the graphic representation of the periodic law.

2.6.1 Spiral Forms

By far, the most popular forms of the periodic table are spirals and tables. Mendeleev only drew a handful of spiral forms and only one was these was published, though it looks more like a table than a spiral (Fig. 2.2) because it omits the elements that would furnish transitions that would connect the bottom of some columns to the top of the next ones [40]. It was, perhaps, meant to be a three-dimensional or screw-shaped spiral rather than a flat, two-dimensional spiral [67]. In 1870, after reading the works of Mendeleev and Meyer, the Swiss chemist Heinrich Baumhauer suggested that the periodic law could be represented in the form of a spiral. By arranging the elements in order of atomic weight, with hydrogen in the center of the spiral, a clear view of the elements could be obtained, he said [68]. Mendeleev was dismissive of Baumhauer’s spiral, claiming it was the spiral table from his paper and that Baumhauer’s arrangement had “little application” and was “artificial” [69].

John Russell Smith suggested that Mendeleev’s dismissiveness toward Baumhauer’s spiral was due to his “failure in early 1871 to draw up a satisfactory spiral arrangement of the elements.” Mendeleev also mentioned spiral arrangements several times, so he was not entirely against them. However, he only found certain types of spirals to be useful ones. In lectures in 1889–90, he said that the periodic law “may be represented in the form of a spiral, where each turn will express a definite period. It may also be represented in the form of a screw-shaped line, where each turn of the screw will represent a period” [70]. And that was, of course, the important aspect—the periods were definite.

Li	Na	K	Cu	Rb	Ag	Cs	—	Tl
7	23	39	63,4	85,4	108	133		204
Be	Mg	Ca	Zn	Sr	Cd	Ba	—	Pb
B	Al	—	—	—	Ur	—	—	Bi?
C	Si	Ti	—	Zr	Sn	—	—	—
N	P	V	As	Nb	Sb	—	Ta	—
O	S	—	Se	—	Te	—	W	—
F	Cl	—	Br	—	J	—	—	—
19	35,5	58	80	190	127	160	190	220.

Fig. 2.2 The spiral table from Mendeleev's 1869 paper. Reproduced from Mendeleev (1869) [40]

Mendeleev did not look upon other curved forms as favorably. Of Lothar Meyer's popular atomic volume curve, Mendeleev commented [71, 72][11]:

> This method, although graphic, has the theoretical disadvantage that it does not in any way indicate the existence of a limited number of elements in each period. … The actual periodic law does not correspond with a continuous change of properties, with a continuous variation of atomic weight.

Forms that did not represent the periods—curves, spirals, two-dimensional, or three-dimensional—were not, in Mendeleev's view, true graphic representations of the periodic law.

2.6.2 Tabular Forms

Tabular forms, that is forms with columns and rows, had an advantage in that the periods were easily shown. Aside from a handful of attempts at spirals, all of the periodic tables that Mendeleev drew were tabular. He drew tables in which the periods were represented in vertical columns and the groups in horizontal rows, and vice versa. The famous first attempt of 1869 is an example of a table with vertical periods while the table from his 1871 paper has horizontal periods.

Mendeleev also drew short-form or long-form tables. In short-form tables, the periods double back (as in the 1871 table) whereas in long-form tables, the periods extend across the table (as in most of the periodic tables you will find in a textbook or on a wall chart today). Until the 1920s, the short-form was the most popular type of periodic table. That began to change with the more complete understanding of the structure of the atom and the change to arranging the periodic table by atomic

[11]Mendeleev had noticed periodicity in atomic volume; see Girolami and Mainz [72].

Gruppen	Reihen: 1	2		4	6	8	10	12
I.		Li = 7		K (39)	Rb (85)	Cs (133)	—	—
II.		Be = 9.2		Ca (40)	Sr (87)	Ba (137)	—	—
III.		B = 11		? Sc [1])	Yt (89 ?)	? Di (139 ?)	Er (175 ?)	—
IV.		C = 12		Ti (48)	Zr (90)	Ce (141)	? La (180 ?)	Th (231)
V.		N = 14		V (51)	Nb (94)	(? [2])	Ta (182)	—
VI.		O = 16	Typische Elemente	Cr (52.5)	Mo (96)	?	W (184)	Ur (240)
VII.		F = 19		Mn (55)	—	—	—	—
				Fe (56)	Ru (103)	—	Os (194 ?)	—
VIII.				Co (58.6)	Rh (104)	—	Jr (195 ?)	—
				Ni (58.6)	Pd (106)	—	Pt (197)	—
I.	H = 1	Na = 23		Cu (63.5)	Ag (108)	—	Au (197)	—
II.		Mg (24)		Zn (65)	Cd (112)	[3])	Hg (200)	—
III.		Al (27.3)		Ga (69)	Jn (113)	—	Tl (204)	—
IV.		Si (28)		? ? ?	Sn (118)	—	Pb (204)	—
V.		P (31)		As (75)	Sb (120) [4])	—	Bi (208)	—
VI.		S (32)		Se (79)	Te (125 ?)	—	—	—
VII.		Cl (35.5)		Br (80)	Jod (127)	—	—	—
	Reihen	3		5	7	9	11	

St. Petersburg, 4./16. April 1880.

Fig. 2.3 The long-form table from Mendeleev's 1880 paper on the history of the periodic law. Reproduced from Mendelejeff (1880) [76]

number rather than atomic weight. By the 1950s, the long-form table had overtaken the short-form in textbooks [73], though short-form tables remained in some classrooms at least into the 1970s.

Mendeleev's opinion regarding which form—short or long—was the best way to represent the periodic system changed. According to Smith, Mendeleev initially preferred the long-form arrangement but after 1869 began to favor the short-form. However, after a decade, Mendeleev again showed a preference for long-form tables [74]. In a short history of the periodic law written in 1880, Mendeleev included a long-form table. This sort of table, he wrote, was the tabular arrangement that he considered "to be the best and most complete expression of the harmony of the elements or of the periodic law (and the most convenient with respect to typography)" (Fig. 2.3) [75]. However, Mendeleev did not abandon the short-form and continued to draw updated versions, such as the one in the 7th edition of the *Principles of Chemistry* that incorporated the newly discovered noble gases (Fig. 2.4) [76].

Short-form and long-form tables had different advantages. Mendeleev believed that the advantage of the long-form table lay in its ability to better show the periodicity of physical properties, such as atomic volume, and to better show analogies between elements. Short-forms, on the other hand, better illustrated the valency of the elements and brought together sub-groups on the basis of the similarity of their compounds. But, as Bensaude-Vincent put it, "Mendeleev never considered one single representation because none of them was totally satisfying" [66]. The only form Mendeleev showed a definite preference for was the tabular form as it showcased the essence of the periodic law—periodicity.

PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES.

Series	GROUPS OF ELEMENTS								
	0	I	II	III	IV	V	VI	VII	VIII
1	—	Hydrogen H 1·008	—	—	—	—	—	—	
2	Helium He 4·0	Lithium Li 7·03	Beryllium Be 9·1	Boron B 11·0	Carbon C 12·0	Nitrogen N 14·04	Oxygen O 16·00	Fluorine F 19·0	
3	Neon Ne 19·9	Sodium Na 23·05	Magnesium Mg 24·3	Aluminium Al 27·0	Silicon Si 28·4	Phosphorus P 31·0	Sulphur S 32·06	Chlorine Cl 35·45	
4	Argon Ar 38	Potassium K 39·1	Calcium Ca 40·1	Scandium Sc 44·1	Titanium Ti 48·1	Vanadium V 51·4	Chromium Cr 52·1	Manganese Mn 55·0	Iron Cobalt Nickel Fe Co Ni (Cu) 55·9 59 59
5		Copper Cu 63·6	Zinc Zn 65·4	Gallium Ga 70·0	Germanium Ge 72·3	Arsenic As 75	Selenium Se 79	Bromine Br 79·95	
6	Krypton Kr 81·8	Rubidium Rb 85·4	Strontium Sr 87·6	Yttrium Y 89·0	Zirconium Zr 90·6	Niobium Nb 94·0	Molybdenum Mo 96·0	—	Ruthenium Rhodium Palladium Ru Rh Pd (Ag) 101·7 103·0 106·5
7		Silver Ag 107·9	Cadmium Cd 112·4	Indium In 114·0	Tin Sn 119·0	Antimony Sb 120·0	Tellurium Te 127	Iodine I 127	
8	Xenon Xe 128	Cæsium Cs 132·9	Barium Ba 137·4	Lanthanum La 139	Cerium Ce 140	—	—	—	— — —
9		—	—	—	—	—	—	—	
10	—	—	—	Ytterbium Yb 173	—	Tantalum Ta 183	Tungsten W 184	—	Osmium Iridium Platinum Os Ir Pt (Au) 191 193 194·9
11		Gold Au 197·2	Mercury Hg 200·0	Thallium Tl 204·1	Lead Pb 206·9	Bismuth Bi 208	—	—	
12	—	—	Radium Rd 224	—	Thorium Th 232	—	Uranium U 239		
HIGHER SALINE OXIDES	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
HIGHER GASEOUS HYDROGEN COMPOUNDS					RH_4	RH_3	RH_2	RH	

Fig. 2.4 The short-form table from the 7th edition of Mendeleev's *Principles of Chemistry*. Reproduced from Mendeléeff (1905) [76]

2.7 Conclusion

The periodic law, as formulated by Mendeleev, was: "The properties of the elements (and of the simple and compound substances which they form) show a periodic dependence on their atomic weights." As seen, periodicity was an important aspect and it influenced Mendeleev's opinions on the best ways to represent the law graphically. Tabular forms were best to illustrate the periods, whereas most spiral forms did not show definite periods. Another important aspect of Mendeleev's periodic system was its use in changing atomic weights of already known elements and in predicting the characteristics of yet-to-be discovered ones. The changes and predictions showcased the utility of the periodic law. And Mendeleev's philosophical conception of chemical elements assisted in the development of the periodic law by allowing him to consider atomic weight as the essential part of the element upon which the law rested.

Just as Ladenburg had told his audience about natural laws, the periodic law did not suddenly spring out of the mind of Mendeleev. He was assisted by "the stock of generalisations and established facts" that had accumulated over decades as chemists sought different ways of determining relationships between the elements, determining atomic weights, and organizing and classifying the elements. These established facts combined with Mendeleev's own understanding of the elements to develop an organizational scheme that encompassed all of the elements, that was flexible enough to survive changes in chemical and physical knowledge, and was useful in both research and pedagogy.

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