D. I. MENDELEEV'S CONCEPT OF CHEMICAL ELEMENTS AND *THE PRINCIPLES OF CHEMISTRY*

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Introduction: Mendeleev's Textbook, *The Principles of Chemistry*

Dmitrii Ivanovich Mendeleev (1834-1907) was primarily a chemist even though he later worked in many other fields. One of his most important contributions to chemistry was the discovery in 1869 of the periodic law of the chemical elements, which is still a fundamental concept in modern chemistry. In 1905, shortly before his death, he listed what he considered his four main contributions to science (1): the periodic law, the elasticity of gas, the understanding of solutions as associations, and *The Principles of Chemistry* (hereafter referred to as *Principles*). Mendeleev himself stated the close relationship between the first and fourth contributions in his first paper on the discovery of the periodic law, written in early March of 1869 (2,3):

> In undertaking to prepare a textbook called 'Osnovy khimii' [*Principles*], and to reflect on some sort of system of simple bodies in which their distribution is guided not by chance, as might be thought instinctively, but by some sort of definite and exact principle.

Few outside Russia, however, have pointed to the direct relationship between *Principles* and the periodic law (4). In Russia B. M. Kedrov (1903-1984), who made a very detailed analysis of Mendeleev's discovery of the periodic law, has discussed this close relationship. In the late 1940s he found new archival material related to Mendeleev's first periodic table, and in the 1950s he published reliable source books on Mendeleev's discovery. His work culminated in his book *The Day of a Great Discovery* (5) in 1958, a very detailed analysis of Mendeleev's process of compiling his first periodic table. All subsequent works on this topic have begun from this work (6). From a critical examination of Kedrov's works, the author has also published a book on Mendeleev's discovery, considering social, as well as scientific, factors (7). All recent studies have included a consideration of this direct relationship between *Principles* and the periodic law (8). However, there are no studies that consider the background of Mendeleev's writing of *Principles* and the changes made in subsequent editions (9). The purpose of this paper is to analyze the text of the first and later editions of *Principles* with its background and show the role played by Mendeleev's concept of the chemical elements in the discovery of the periodic law and its later development.

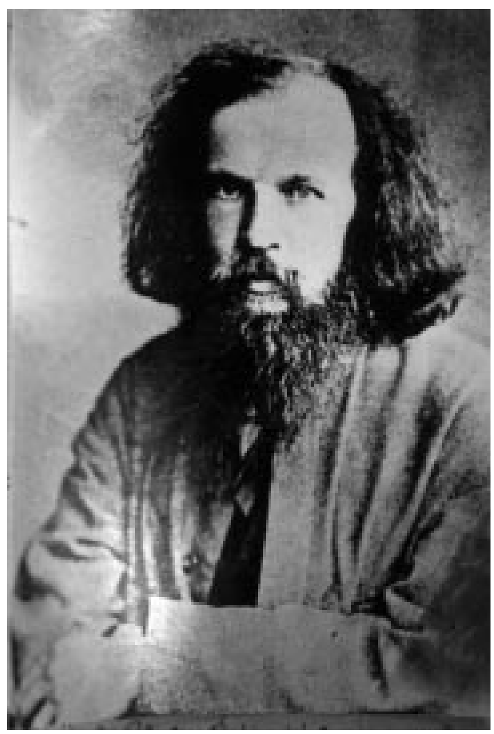
Origin of Mendeleev's Concept of the Chemical Elements and So-called Indefinite Compounds

Mendeleev entered the Main Pedagogical Institute at St. Petersburg in 1850 after graduating from the gymnasium in the Siberian city of Tobol'sk, where he was born in 1834. While a student, he published his first scientific papers on the chemical analysis of minerals from Finland (10). His undergraduate thesis was on isomorphism and was concerned with the development of mineral analysis (11). Even this thesis foreshadows Mendeleev's future line of research: first, it shows his talent for compiling and systematizing large amounts of data; second, it mentions Auguste Laurent (1808-

1853) and Charles Gerhardt (1816-1856), the reformers of chemistry in the 1840s and 1850s (12); and third, its theme, the relationship between similarities of crystal form and composition, made Mendeleev seriously consider the problem of the similarity of substances. I think this was the beginning of his involvement with the problem of classifying substances.

Mendeleev taught briefly at gymnasiums in southern Russia before returning to the capital to receive a master's degree and become a lecturer at St. Petersburg University. His master's thesis on specific volumes illustrates his later line of thought even more clearly (13). He adopted the atomic weight system of Gerhardt and Laurent and Avogadro's hypothesis (which Mendeleev called Gerhardt's law). This thesis also shows Mendeleev's interest in the natural classification of substances based on their specific volume.

In April 1859 Mendeleev went to Western Europe to study. During his two-year stay in Europe he studied the "cohesion" of various substances (the forces holding their molecules together), especially of organic compounds, through capillary phenomena. He tried to find a universal formula to explain the relationship of cohesion expressed in terms of surface tension with composition, density, or molecular weight. The instruments that Mendeleev purchased in Heidelberg, Bonn, and Paris enabled him to measure the properties of substances with very good precision. In September 1860 he attended the International Congress of Chemists in Karlsruhe, which considered significant contemporary issues in chemistry, especially atomic weights. Along with everyone else in attendance, Mendeleev received a copy of the famous paper on the new atomic-weight system by Stanislao Cannizzaro (1826-1910), who distributed it at the meeting (14). Immediately after reading the paper, Mendeleev wrote to his teacher A. A. Voskresenskii (1808-1883) in St. Petersburg with an informative report on both the Congress and the content of Cannizzaro's paper. His letter was published in a St. Petersburg newspaper and in a Moscow journal that same year (15). In pointing out the inconsistency of Gerhardt's atomic weights of metals and arguing that Cannizzaro corrected them with the "multiatomicity of metals," Mendeleev clearly recognized Cannizzaro's successful system of atomic weights. In his letter to Voskresenskii, Mendeleev showed that, for various substances, the atomic heat (i.e., the product of specific heat and atomic weight) divided by the substance's number of atoms results in a constant (about 6-7). Thus, Cannizzaro's atomic weights were found to be in accord with the law of Dulong and Petit.



Mendeleev, 1878

Early in 1861 Mendeleev returned to Russia. That same year, while teaching at various schools, he completed his first chemistry textbook, *Organic Chemistry*. In this he was already seeking "some sort of definite and exact principle" as a guide, like that later in *Principles*, finding it in what he called "the theory of limits" (16). This was the classification of organic compounds on the basis of their degree of saturation and their substitution reactions. Although this theory would soon be forgotten because of the advent of the structural theory of organic compounds, Mendeleev's textbook was well received in Russia. In 1862 the St. Petersburg Academy of Sciences awarded him the Demidov Prize for the outstanding book written in Russian during the previous year. In this textbook Mendeleev followed Cannizzaro's principle for determining atomic weights and defined them as "the minimum quantity of an element in the compound molecules of the element" (17). He also explicitly distinguished between "bodies" and "radicals," terming the former "something divisible (molecule)" and the latter "the theoretical notion" and "indivisible whole (atom)" (18).

After completing his textbook of organic chemistry, Mendeleev intended to write a textbook on inorganic and theoretical chemistry. He tried to extend the idea of saturation (his "theory of limits") to inorganic compounds, but with little success (19). He also left an 1864 lecture notebook on theoretical chemistry (20).

I believe that Mendeleev made one more change in his line of thought on atomic weights during 1860s. Even before his acquaintance with Cannizzaro's paper, Mendeleev had been especially concerned with deviations from the law of definite proportions. In his 1856 habilitation dissertation, he discussed the structure of silicate compounds (21), arguing that such compounds must be a kind of "alloy" of oxides, because, like alloys, "to some extent they can vary their composition (and formula) without changing their forms and main properties" (22). He developed this line of research, calling substances that had constant physical properties, but varied composition—such as solutions, alloys, isomorphous mixtures, and silicate compounds—"indefinite compounds." Such compounds had been studied very little, and Mendeleev himself could not explain their formation in any proper way. However, he emphasized the following points: they are not simply physical mixtures; some chemical power must be involved in their formation; and they show some properties that are similar to those of definite compounds (23). His doctoral thesis "On Compounds of Alcohol with Water," submitted in 1865, can be regarded as a study of solutions that arose from his interest in so-called indefinite compounds (24).

Russian Chemists in Heidelberg in 1859-1860: (left to right) N. Yitinskii, A. P. Borodin, Mendeleev, V. I. Olevinskii

Underlying this interest was Mendeleev's concern that the formation or composition of indefinite compounds was difficult to explain in terms of the atomic theory, which was based on the concept of definite proportions. Even though no previous writers have emphasized the idea that Mendeleev was moving away from a belief in the atomic theory in this period (1864-1868), Mendeleev himself made this point clear in a lecture on theoretical chemistry published in 1864 (25):

In fact, although on the one hand, the law of definite chemical compounds has persuasively proven the atomic theory, on the other hand, a whole group of compounds, the so-called indefinite compounds, have shown evidence, which is directly against the theory.

Almost the same passage appears in the first part of the first edition of *Principles* (26):

> [C]ompounds with indefinite compositions . . . speak against the atomic doctrine as much as definite chemical compounds speak in its support.

It is important to note that Mendeleev paid very little attention to atomic weights in the first part of this new textbook. He mentioned the atomic weights of only some 22 of the most familiar elements (27). It is true that a table of the 63 elements then known appears in the second chapter of the first part, but the elements are arranged alphabetically with no mention of their atomic weights (28). It seems likely that the existence of indefinite compounds made Mendeleev accept the limitation of the atomic theory and the narrow scope of atomic weights (29).

Even as Mendeleev regarded atomic theory with caution because of exceptions to the law of definite proportions, he insisted on the existence of distinct chemical elements, which were clearly distinguished from simple bodies. He argued this point in his first series of lectures at St. Petersburg University in the fall of 1867 (30):

> [I]t is necessary to distinguish the concept of a simple body from that of an element. A simple body substance, as we already know, 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. An element, on the other hand, is an abstract concept; it is 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.

A similar definition of element and the same argument for the need to distinguish clearly between element and simple body were later presented in the first part of *Principles* (31).

Thus, this distinction between "simple bodies" and "elements" is essentially the same as that between "bodies" and "radicals" in Mendeleev's 1861 organic chemistry textbook, but without any mention of atoms or molecules. Paradoxically, then, it appears that Mendeleev was led to the weight of elements as an invariable characteristic and hence to his periodic system, not by adherence to the concept of chemical atoms, but by seeking freedom from it, as the failures of the law of definite proportions seemed to demand. It is reasonable to suppose that he refined the concept of the elements to bear an attribute of an individual chemical entity without employing the notion of atoms because of the supposed limitations of the atomic theory.

During the 1860s the theory of valence enjoyed great success, helping in the development of a new theory of organic chemistry, i.e., a structural theory of organic compounds. After Mendeleev wrote his textbook of organic chemistry based on a pre-structural theory, his "theory of limits," it seems that he tentatively took the valences of the elements as a basic principle in writing his inorganic chemistry textbook, *Principles*, at the end of the 1860s, because of the success of valence theory in organic chemistry. But without the assumption of atoms, valence was incomprehensible. Hence Mendeleev had to look further for "some sort of definite and exact principle." He had to find a fundamental property of the elements. Out of this exigency, weight—which we think of as "atomic," but Mendeleev thought of as "elementary"—took on a new and increased importance.

The Social Background of Mendeleev's Writing of *The Principles of Chemistry*

Before analyzing the relationship between *Principles* and the discovery of the periodic law, let us briefly examine the social background of the writing of *Principles*. Published between 1868 and 1871, *Principles* grew out of Mendeleev's need for a suitable textbook on chemistry in Russian, which was lacking when he began teaching at St. Petersburg University in the fall of 1867 as the Professor of General Chemistry (32):

> I began to write [*Principles*] when I started to lecture on inorganic chemistry at the university after [the departure of] Voskresenskii and when, having looked through all the books, I did not find anything to recommend to students.

Mendeleev had obtained the position of a permanent lecturer at St. Petersburg University in 1864. He became an extraordinary professor of technical chemistry the following year and was promoted to full professor at the end of the same year. In the fall of 1867 Mendeleev was transferred to the professorship of general chemistry to succeed Voskresenskii, his own teacher, who left the university that year.

Mendeleev's research career in chemistry, which began in 1854, reached its first zenith with the discovery of the periodic law in 1869. This discovery can also be considered the culmination of his social activity during this period. Those years, beginning in the middle of the 1850s after the Crimean War and running their course by the 1860s with the emancipation of the serfs in 1861, constituted a period of great change and reform in Russia. This was the second attempt at social and economic change after the social and political reforms of Peter the Great in the early 18th century; it has been called by

Table 1. BOOKS PUBLISHED WITH MENDELEEV AS AUTHOR OR EDITOR

1861	*Organic Chemistry*, 1st edition
1862	*Cahours' Textbook for Elementary General Chemistry*, second pt. (translation)
	Wagner's Technology (1862-1869), 8 Vol. (translation and compilation)
1863	*Organic Chemistry*, 2nd edition
1864	*Gerhardt and Chancel's Analytical Chemistry, Qualitative Analysis* (translation)
1866	*Analytical Chemistry*, second pt., Vol. 1-3 (1866-1869)
1867	*Today's Development of Some Chemical Productions—From the Point of View for the Application to Russia* (Report of International Exposition at Paris in 1867)
1868	*The Principles of Chemistry*, first pt., first vol.

Table 2. CHRONOLOGY OF THE PUBLICATION OF THE FIRST EDITION OF *PRINCIPLES* AND DISCOVERY OF THE PERIODIC

DATE	PUBLICATION
May-June 1868	*Principles*, first volume (part 1, chapters 1-11)
February 17, 1869	"An Attempt at a System of the Elements Based on Their Atomic Weight and Chemical Affinity" (the first periodic table)
March 6, 1869	"The Correlation of the Properties and Atomic Weights of the elements" (the first paper on the periodic law, Paper I)
March 1869	*Principles*, second volume (part 1, chapters 12-22).
February-March 1870	*Principles*, 3rd volume (part 2, chapters 1-8).
February 1871	*Principles*, 4th & 5th volumes (part 2, chapters 9-23).
July 1871	"The Periodic Law of the Chemical Elements" (in *Annalen der Chemie und Pharmacie*, Paper II)

some historians "the Great Reforms Era." It was also a time of change in chemistry: the dispute over the merits of different atomic weight systems had finally been settled after the Karlsruhe Congress; and classical organic structural theory had appeared.

The emergence of a new generation of chemists in Russia, eager to engage in original laboratory work and pursue a European trend in chemistry, was the important background to Mendeleev's activities in this period. The educational system, especially at the higher levels, was also reorganized during this time. Because of the large numbers of Russian chemists moving into posts at academic institutions, the Russian Chemical Society was organized in 1868, Mendeleev being one of the founding members.

Let us consider the objectives that Russian chemists, including Mendeleev, were expected to achieve during this period. They consisted of the practical and the theoretical. The practical objective was to educate qualified professionals for the new capitalistic production that Russia required. The theoretical objective was to deal with current theoretical and experimental problems in chemistry to meet the needs of the time, as the classical foundations of chemistry were being established. Mendeleev was aware of these objectives. In his *Principles* he answered not only the theoretical requirements, but also the practical ones.

This point is illustrated by a listing of the books Mendeleev published during the 1860s after his return from Europe (Table 1). The contents of these books indicate that they all met the practical demands of Russian society. *Wagner's Technology*, for example, was initially the translation of German encyclopedic manuals on technology. As the editor, Mendeleev proposed to translate the pertinent sections needed in Russia, i.e., the parts on agricultural products and processing. Later on, he added the translations from other related books and also asked appropriate specialists to write original texts. They were all issued by the same publisher, "Obshchestvennaia pol'za" ["Social Benefit"], a company that produced books and pamphlets on science and technology for the "social benefit and enlightenment of the people" (33). *Principles*, offering an advanced method for systematizing inorganic chemistry, was the new textbook for higher education urgently needed by Russian society. Mendeleev's famous textbook was the culmination of his work to help satisfy his country's needs during that period.

The Principles of Chemistry and the Discovery of the Periodic Law

First, let us consider the chronology of the publications of the first edition of *Principles* and the discovery of the periodic law (Table 2). In May or June 1868, Mendeleev published the first volume (Chapters 1-11). On February 17, 1869 (34), he compiled the first periodic table, titled "An Attempt at a System of the Elements Based on Their Atomic Weight and Chemical Affinity" (35).

On March 6, N. A. Menshutkin (1842-1907), the secretary of the recently established Russian Chemical Society, read Mendeleev's first paper on his discovery, "The Correlation of the Properties and Atomic Weights of the Elements" (Paper I) (36) at a meeting of the society. At almost the same time, Mendeleev published the second volume of *Principles*, Chapters 12-22. At the end of February or early in March 1870, the third volume, which comprises Chapters 1-8 of Part 2, appeared. Finally, the last volumes (the fourth and fifth), which include Chapters 9-23, were published in February 1871. In July of that year, his most comprehensive paper on the periodic law, "The Periodic Law of the Chemical Elements," was published in a supplemental volume of the *Annalen der Chemie und Pharmacie* (Paper II) (37). This chronology (Table 2) makes it clear that Mendeleev discovered the periodic law in the middle of writing *Principles*. As Kedrov has pointed out, a careful reading of this text reveals exactly when he discovered that law (38).

Let us examine Mendeleev's first paper on the periodic law (Paper I) and the early chapters of the second part of his textbook, which must have been written around the same time. He organized the first part of *Principles* on the basis of the principle of valence: first he discussed univalent hydrogen, then divalent oxygen, trivalent nitrogen, and tetravalent carbon (39). After his treatment of the univalent halogens, which concludes the first part of the textbook, Mendeleev began the second part with a description of the univalent alkali met-

Table 3. DIFFERENCES BETWEEN THE THIRD/FOURTH AND FIFTH EDITIONS OF *PRINCIPLES*

Third/Fourth Editions	Fifth Edition
chapters	chapters and elements [group number]
1 & 2	Introduction
3 & 4	1: H_2O
5	2: H_2O, H [I]
6 & 7	3: O [II]
9 & 10	4: O_3, H_2O_2
11	5: N [III]
12 & 13	6: N with H &O
14	7: Molecules and Atoms
15 & 16 & 19	8: C & Hydrocarbons [IV]
17 & 18	9: C with O & N
20	10: NaCl, HCl [VII]
21 & 22	11: Cl, Br, I, F [VII]
23	12: Na [I]
24	13: K, Rb, Cs, Li [I]
25 & 26	14: Mg, Ca, Sr, Ba, Be [II]
27	15: "The Similarity of the Elements and the Periodic Law"
28	16: Zn, Cd, Hg [II]
29 & 30 & 31	17: B, Al,Ga, In, Tl [III], the rare earths
32 & 33	18: Si, Ge, Sn, Pb [IV]
34 & 35	19: P, As, Sb, Bi, V, Nb, Ta [V]
36 & 37 & 38	20: S, Se, Te [VI]
39	21: Cr, Mo, W, U [VI], Mn [VII]
40 & 41	22 Fe, Co, Ni [VIII]
43	23 Or, Ir, Pt, Pd, Rh, Ru [VIII]
42 & 44	24: Cu, Ag, Au [I]

als. At the end of the chapter on heat capacity, which follows the alkali metals, he explained that he would next treat the alkaline-earth metals, which are divalent and not analogs of copper, which awkwardly exhibits both univalence and divalence (40). Although he had followed the principle of valence to this point in the textbook, he abruptly began the next chapter from a different perspective: a comparison of the alkaline-earth metals with the alkali metals on the basis of their atomic weights. In this connection, it should be noted that toward the end of Paper I, Mendeleev stressed that (41):

> [T]he purpose of my paper would be entirely attained if I succeed in turning the attention of investigators to the relationships in the size of the atomic weights of *nonsimilar* elements, which have, as far as I know, been almost entirely neglected until now.

He emphasized the word "nonsimilar" with italics. Alkali metals and alkaline-earth metals were obviously such nonsimilar groups of elements.

If Kedrov's analysis in *The Day of a Great Discovery* (42) of Mendeleev's process is followed, then Mendeleev noticed this comparison of nonsimilar groups of elements in the middle of February 1869; and he first compiled the central part of the table on the basis of this principle. With the help of cards of the chemical elements, which he made for this occasion, Mendeleev finally succeeded in organizing a table of all the known elements on the basis of their atomic weights. He completed this on February 17, 1869 (43). Clearly, at that moment, Mendeleev had conceived the idea that atomic weight might be the fundamental numerical property of the elements.

> In Paper I Mendeleev wrote (44): No matter how properties of simple bodies may change in the free state, *something* remains constant, and when the element forms compounds, this *something* is material existence and establishes the characteristics of the compounds, which include the given element. In this respect we know only one constant peculiar to an element, namely the atomic weight. The size of the atomic weight, by the very essence of matter, is common to the simple body and all its compounds. Atomic weight belongs not to coal or diamond, but to carbon.

This "something," italicized in the quotation above, corresponds exactly to Mendeleev's definition of element. In other words, atomic weights belong to elements!

Mendeleev in St. Petersburg, Nov. 19, 1861

As a result of this reconceptualization or discovery, Mendeleev realized that he should use atomic weights, not valence, as the guiding principle for the remainder of his textbook. This was the moment when he started to write the chapter on alkaline-earth metals. However, since he defined the concept of element without the notion of atoms, he considered atomic weights to be the fundamental property of the elements. They were not necessarily based on atomic theory, which was still somewhat speculative. Thus, the scope of atomic weights would have to be broader than that of definite proportions on which the atomic theory was thought to be based. Mendeleev even once suggested the use of the word "elementary weight" instead of "atomic weight" (45).

Changes in Later Editions of *The Principles of Chemistry*

Contrary to many statements in the existing literature on the periodic law—that Mendeleev kept the original version of *Principles* unchanged through subsequent edition—(46), he actually revised the structure of the textbook significantly with each new edition. Much confusion has resulted from this misunderstanding. In all, eight editions were published during Mendeleev's lifetime. Let us look briefly at some of the changes in ensuing editions of *Principles*.

There were two type fonts in the text of the first four editions: sections in a larger font for beginning students and those in a smaller font for advanced learners. In the second edition, published in 1872-1873, just one year after the completion of the first, there were only minor changes in the text. Mendeleev moved indium and uranium to the appropriate chapters because of the improved values of their atomic weights. He also changed the positions of the rare earths, which remained problematic throughout his life (Fig. 1).

The third edition, which appeared in 1877, underwent substantial change; and the chapters were completely reorganized in accord with the periodic law. The textbook was divided into two parts, as were the first two editions, but the chapters were now numbered successively throughout. Only small changes were needed in the first part, which was introductory and devoted to the elements frequently encountered in daily life. Mendeleev placed the chapter on the periodic law, entitled "Similarity of Elements and Their System," in the second part, immediately after the description of the alkali and alkaline-earth metals. After these chapters he described the elements in order of their position in the periodic table: from the second group to the sixth group, ending with the eighth group, iron and platinum analogs. The final chapters were devoted to the noble metals. The third edition also included gallium, the first of the elements to be discovered after Mendeleev had predicted their existence.

The fourth edition in 1881-1882 was the same as the third in organization but slightly larger, increasing in size from 18 x 11 cm to 20 x 12 cm. Mendeleev first mentioned the discovery of scandium in this edition.

The fifth edition of 1889 underwent the second major change after the third edition. It was considerably larger, and for the first time the text was printed in double columns rather than in single columns. Therefore, the whole work became much shorter, reduced from 1176 pages
in the fourth edition to 789 pages in the fifth. Some of the material from previous editions was moved into the footnotes in smaller font. There were no longer two parts, only one, bound as a single volume, a format retained in all subsequent editions. The chapters were also completely reordered. Many of them were combined, and the 44 chapters in the fourth edition became only 24 chapters in the fifth (see Table 3). The chapter on the periodic law was expanded to include the history of its discovery and the problem of priority (47). This fifth edition was translated into English, German, and French (48).

The sixth edition of 1895 was essentially unchanged in format from the fifth, but Mendeleev revised many of the footnotes. He added notes on argon, the newly

Table 4. MENDELEEV'S AND BRAUNER'S ARRANGEMENTS OF THE ELEMENTS (both from the 7TH Russian Edition, 1902

Mendeleev's arrangement [copy from the 7th Russian edition]

Mendeleev's arrangement, 1902

	Groups of Elements								
Rows	0	I	II	III	IV	V	VI	VII	VIII
8	Xe	Cs	Ba	La	Ce	---	---	---	--- --- ---
9		---	---	---	---	---	---	---	
10	---	---	---	Yb	---	Ta	W	---	Os Ir Pt

Brauner's arrangement, 1902 [copy from the 7th Russian edition]

Brauner's arrangement, 1902

Groups:	0	I	II	III	IV	V	VI	VII	VIII
8th-Row	Xe	Cs	Ba	La	Ce etc.	Ta	W	---	Os Ir Pt

wherer Ce etc. = Ce Pr Nd Sm Eu Gd Tb Ho Er Tu Yb discovered gas from the air, at the end of the textbook, and he argued for the possibility that argon might be N_3.

By the seventh edition of 1902-1903 Mendeleev had abandoned N_3 and fully accepted the noble gases, which he incorporated into the chapter on nitrogen and air. Mendeleev asked the Czech chemist Bohuslav Brauner (1855-1935) to write the section on the rare earths for the seventh and eighth editions, even though they had somewhat different opinions on the positions of these elements within the periodic system. They agreed to place scandium, yttrium, and lanthanum in the third group and tantalum in the fifth. However, while Mendeleev believed that future research would reveal sufficient numbers of rare earth elements with different properties, so they could be placed in different groups to fit neatly into his periodic table, Brauner proposed that the rare earths should be all placed together in group IV, which was formerly occupied by cerium alone (Table 4). Effectively, this demonstrates Mendeleev's admission of the difficulties in placement of the rare earths, so many in number and so similar in properties, within his periodic system. He also mentioned the discovery of radium in this edition, but denied the possibility of the transformation of the elements. He suggested other possible explanations of radioactivity, such as a "state" like a magnetic property or an absorbency and the projection of the "ether" in the vicinity of the radioactive atom.

The eighth edition in 1906 was the last published before Mendeleev's death. All the notes were separated from the main text and placed in the second half of the book. He argued for the possibility of a "chemical ether" as an extremely light element in the noble gas group, which he thought could explain radioactivity (49).

Members of the Chemistry Section of the First Congress of Russian Naturalists (front row, 5th from left, A. A. Voskresenskii; back row, 2nd from right, Mendeleev; 6th from right, N. A. Menshutkin

As shown in his textbook, Mendeleev's concept of the chemical elements demonstrates his firm and persistent belief in their conceptual priority. His clear understanding of the elements is evident from the very first edition. In his concept of an element, Mendeleev clearly departed from Lavoisier, who had offered a negative definition of an element as an undecomposed substance. For Mendeleev, the concept was defined positively as something abstracted from the diverse properties of simple bodies and their compounds. Therefore, elements were strictly distinguished from simple bodies.

Beginning with the first edition of *Principles*, Mendeleev carefully denied the speculative connotations of the atomic hypothesis. Although it is tempting to say that his "element" is a substitute for "atom," Mendeleev resisted the use of the hypothetical atom. He was also opposed to any suggestion that served to reduce simple substances to a single substance or a few substances called "primary matter" (50). This attitude was in sharp contrast to those of other individuals who also sought a system of the elements during the 1860s (51).

Lothar Meyer's Approach to the Classification of the Elements

Let us briefly consider the case of Lothar Meyer (1830-1895) as an example of the "reductionist" tendency (52). His paper, "The Nature of the Chemical Elements as a Function of their Atomic Weights," appeared early in 1870 (53). He began with speculation related to Prout's hypothesis (54). On some points he went further than Mendeleev did in 1869 in his Paper I. Meyer succeeded in vividly conveying the periodic dependence of the properties of the elements on their atomic weights by plotting the solid-state atomic volumes of the elements (simple bodies) against their atomic weights (55). Although he admitted in the paper that his table was essentially the same as Mendeleev's, his table of elements was more refined than Mendeleev's first attempt, especially in clearly showing the so-called transition metals. Meyer also had the correct weight of indium, to which Mendeleev had attributed an incorrect weight in his first paper. However, the conclusion of Meyer's paper was very tentative, even timid (56):

> It would be hasty to undertake to alter on such uncertain bases the previously accepted atomic weights. On the whole, one may not attribute any very great weight to arguments of the sort here given, nor expect from them so certain a decision [regarding atomic weight] as is given by determination of the specific heat or the vapor density. They may however serve even now to turn our attention upon doubtful and uncertain assumptions and to challenge us to a renewed testing of them. And again, conversely, this testing will help to clarify and extend the meager beginnings of our knowledge of atoms.

Meyer's conclusion lacks the confidence expressed by Mendeleev in his first paper. In 1869 there was a noticeable difference between these two men in their attitudes toward the concept of the atom. Whereas Mendeleev discarded the atom and relied solely on the refined concept of a chemical element, Meyer embraced the atom and even supported the speculation of Prout's hypothesis of a primordial matter (hydrogen) as the building block of the elements. This prompted Meyer to underestimate his findings and prevented his having full confidence in his discovery of 1869. In 1873, however, Meyer published another paper (57), in which he fully applied the periodic law, citing Mendeleev's comprehensive 1872 paper on the subject (Paper II in Table 2) as the evidence for the validity of his own work.

Conclusion: Mendeleev's Concept of the Chemical Elements and 19th-Century Chemistry

Mendeleev's concept of the chemical elements as a stable, intermediate level of matter, not necessarily based on the speculative concept of the atom, corresponded to the state of chemistry in the mid-19th century. Ironically, it helped him discover the periodic law. This deep insight, which assured him of the validity of his discovery, allowed him to apply it fully to the chemistry of his time, without being bothered by a seeming regularity in numbers on the one hand, or being misled by a speculative primordial matter on the other. As a result of his discovery, the concept of an element gained another positive characteristic in its definition: an element occupies a specific place in the periodic system (58). Later Mendeleev's concept of chemical elements developed into "chemical individuals," his further attempt to avoid the speculative connotations of the atomic theory (59). Even though the formats of Mendeleev's textbook changed substantially with each edition, his firm belief in the validity of the concept of the chemical elements remained unchanged from the 1860s.

In the course of revising his textbook, Mendeleev developed his concepts further. Eventually, however, he encountered insurmountable difficulties, including the placement of the rare earths in his system (60), abnormalities in the order of atomic weights, and new phenomena, such as radioactivity. These were the predicaments that could be solved only by a new concept of the elements, which was beyond Mendeleev's understanding and that of 19th-century chemistry in general.

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2. This date is in the Julian calendar, used in Russia until January 1918. The Julian calendar lagged 12 days behind the Gregorian calendar in the 19th century and 13 days in the 20th century. In this paper I am using the Julian calendar for events in Russia and the Gregorian dates for events outside Russia.
3. D. Mendeleev, "Sootnoshenie svoistv s atomnym vesom elementov" ["The Correlation of the Properties and Atomic Weights of the Elements"], *Zh. Russ. Khim. Obshch.*, **1869**, *1*, No. 2/3, 60-77 (65). I have used the English translation of this paper, with some modification, from H. M. Leicester and H. S. Klickstein,

Sourcebook in Chemistry 1400-1900, Harvard University Press, Cambridge, MA, 1952, 439-444.

4. Leicester was one of the few historians in the West who clearly pointed out this connection before Kedrov. See, e.g., H. M. Leicester, "Factors which Led Mendeleev to the Periodic Law," *Chymia*, **1948**, *1*, 67-74 (71); also H. M. Leicester, *The Historical Background of Chemistry*, 1956, reprinted Dover Publications, New York, 1971, 193.
5. B. M. Kedrov, *Den' odnogo velikogo otkrytiia* [*The Day of a Great Discovery*], Izd. Sotsial'no-ekonomicheskoi Literatury, Moscow, 1958. His main points are also available in English: B. M. Kedrov, "Dmitry Ivanovich Mendeleev," *Dictionary of Scientific Biography*, C. C. Gillispie, Ed., Charles Scribner's Sons, New York, 1974, Vol. 9, 286-295 (288).
6. For example, I S. Dmitriev's recent paper in Russian on the discovery of the periodic law starts from criticism of Kedrov's analysis and tries to present an alternative version: I. S. Dmitriev, "Nauchnoe otkrytie *in statu nascendi*: periodicheskii zakon D. I. Mendeleeva" ["Scientific Discovery *in statu nascendi*: The Periodic Law of D. I. Mendeleev"], *Vopr. Istor. Estestvozn. Tekh.*, **2001**, No.1, 31-82.
7. M. Kaji, *Mendeleev's Discovery of the Periodic Law of the Chemical Elements—The Scientific and Social Context of His Discovery* [in Japanese], Hokkaido University Press, Sapporo, Japan, 1997.
8. For example B. Bensaude-Vincent, "Mendeleev's Periodic System of Chemical Elements," *Br. J. Hist. Sci.*, **1986**, *19*, 3-17.
9. Loren R. Graham has emphasized the need to study the evolution of Mendeleev's views in later editions of *Principles* more thoroughly. See L. R. Graham, *Science in Russia and the Soviet Union: A Short History*, Cambridge University Press, Cambridge, 1993, 266, note 34. There is a recent study of these aspects by N. M. Brooks, "Dmitrii Mendeleev's *Principles of Chemistry* and the Periodic Law of the Elements," in A. Lundgren and B. Bensaude-Vincent, Ed., *Communicating Chemistry: Textbooks and Their Audiences, 1789-1939*, Science History Publications, Canton, MA, 2000, 295-309. However, Brooks' conclusions are different from mine, especially on the organization of later editions of *Principles*.
10. Reprinted in D. Mendeleev, *Sochineniia* [*Collected Works*], Izd. Akademii Nauk SSSR, Leningrad, 1949, Vol. 15, 16-19, 20-23. Hereafter referred to as *Works*.
11. "Izomorfizm v sviazi s otnosheniiami kristallicheskoi formy k sostavu" ["Isomorphism in the Relationship Between Crystal Form and Composition"], reprinted in *Works*, Vol. 1, 7-137.
12. On the role of Laurent and Gerhardt in the reform of the atomic weight-molecular formula problem, see A. J Rocke, *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro*, Ohio State University Press, Columbus, OH, 1984, 192-214. For their influence in Russia, including that on Mendeleev, see M. G. Faershtein, *Istoriia ucheniia o molekule v khimii (do 1860 g.)* [*The History of Molecular Theory in Chemistry (up to 1860)*], Izd. Akademii Nauk SSSR, Moscow, 1961, 290-321.
13. "Udel'nye ob"emy" ["Specific Volumes"], reprinted in *Works*, Vol. 1, 139-323; Vol.25, 112-228.
14. S. Cannizzaro, "Sunto di un corso di filosofia chimica," *Nuovo Cim.*, **1858**, *7*, 321-366 (1858). For an English translation, see *Sketch of a Course of Chemical Philosophy by Stanislao Cannizzaro (1858)*, Alembic Club Reprint No. 18, Alembic Club, Edinburgh, 1910. This translation is also reprinted in M. J. Nye, *The Question of the Atom: From the Karlsruhe Congress to the First Solvay Conference, 1860-1911*, Tomash Publishers, Los Angeles, CA, 1984, 31-87.
15. Mendeleev's letter to Voskresenskii is reprinted in D. I. Mendeleev, *Periodicheskii zakon* [*The Periodic Law*], B. M. Kedrov, Ed., Izd. Akademii Nauk SSSR, Moscow, 1958, 660-669, and also in N. A Figurovskii, *Dmitrii Ivanovich Mendeleev, 1834-1907*, 2nd ed., Nauka, Moscow, 1983, 274-280.
16. D. Mendeleev, "Essai d'une théorie sur les limites des combinaisons organiques," *Bull. Acad. Imp. Sci. St.-Pétersbourg*, **1862**, *4*, 245-250; reprinted in *Works*, Vol. 8, 22-27.
17. D. Mendeleev, *Organicheskaia khimiia* [*Organic Chemistry*], 1st ed., St. Petersburg, 1861, v.
18. Ref. 17, note on p 36.
19. A. A. Makarenia, *D. I. Mendeleev i fiziko-khimicheskie nauki—Opyt nauchnoi biografii D. I. Mendeleeva* [*D. I. Mendeleev and the Physico-Chemical Sciences—An Attempt at a Scientific Biography of DI. Mendeleev*], 2nd ed., Energoizdat, Moscow, 1982, 92-100.
20. "Fragmenty iz lektsii D. I. Mendeleeva po teoreticheskoi khimii" ["Fragments from D. I. Mendeleev's Lectures on Theoretical Chemistry"], in D. I. Mendeleev, *Izbrannye lektsii po khimii* [*Selected Lectures on Chemistry*], Izd. Vysshaia Shkola, Moscow, 1968.
21. "O stroenii kremnezemistykh soedinenii" ["On the Structure of Silicate Compounds"], a dissertation pro venia legendi, 1856, reprinted in *Works*, Vol. 25, 108-228.
22. Ref. 21, p 220.
23. For his arguments during the 1860s, see Ref. 20, pp 9-69, especially pp 11-14, 26-59.
24. "O soedinenii spirta s vodoi" ["On Compounds of Alcohol with Water"], St. Petersburg, 1865, reprinted in *Works*, Vol. 4, 1-52.
25. Ref. 24, p 24.
26. D. Mendeleev, *Osnovy Khimii* [*The Principles of Chemistry*], 1st ed., Part 1, Ch.10, reprinted in *Works*, Vol. 13, 337.
27. Ref. 26, 1st ed., Part 1, Ch. 10, reprinted in *Works*, Vol. 13, 342.
28. Ref. 26, 1st ed., Part 1, Ch. 2, reprinted in *Works*, Vol.

13, 77-82. The third edition has the same table, but with atomic weights.
29. Ref. 26, 1st ed., Part 1, Ch. 10, reprinted in *Works*, Vol. 13, 340-341.
30. *Lektsii po obshchei khimii 1867/68 g.* [*Lectures on General Chemistry in 1867/68*], Lecture V, St. Petersburg, reprinted in *Works*, Vol. 15, 381-382. A lithographic edition of these lecture notes was found in the library of the former Bestuzhev women's courses, one of the most important institutions of higher education for women in pre-revolutionary Russia. Consisting of sixteen lectures, these notes are similar to the first half of part 1 of *Principles* written in 1868. In the fifth lecture, there is a table of 63 elements, ordered alphabetically by their Latin names. The atomic weights of 12 of these elements were incorrect, which could not have been the case after the discovery of the periodic law. All this evidence shows that these notes are a record of Mendeleev's lectures on general chemistry given at St. Petersburg University in the fall of 1867.
31. Ref. 26, 1st ed., Part 1, Ch. 2, reprinted in *Works*, Vol. 13, 73-74 and also Ch. 15, reprinted in *Works*, Vol. 13, 488-490.
32. Ref. 1, pp 52-53.
33. *Tridtsatipiatiletie vysochaishe utverzhdennogo Tovarishchestva "Obshchestvennaia pol'za"* [*The Thirty-Fifth Anniversary of the Founding of the "Social Benefit" Company*], Obshchestvennaia Pol'za, St. Petersburg, 1895, 5.
34. See the clarification of dates in Ref. 2.
35. D. Mendeleev, "Opyt sistemy elementov, osnovannoi na ikh atomnom vese i khimicheskom skhodstve," ["An Attempt at a System of the Elements Based on Their Atomic Weight and Chemical Affinity"], in Ref. 15, p 9.
36. Ref. 3. Mendeleev was not present for this meeting because he had left St. Petersburg on March 1 for a consulting trip with farmers in cheese-making communities. He was sent by the Free Economic Society (Vol'noe ekonomicheskoe obshchestvo), one of the oldest scientific societies in Russia.
37. D. Mendelejeff, "Die periodische Gesetzmässigkeit der chemischen Elemente," *Ann. Chem. Pharm.*, **1871**, Supplementband, *8*, 133-229. Mendeleev's manuscript was translated into German by Felix Wreden, a friend of Mendeleev in St.Petersburg. The original Russian text was first published in D. I. Mendeleev, *Novye materialy po istorii otkrytiia periodicheskogo zakona* [*New Materials on the History of the Discovery of the Periodic Law*], Izd. Akademii Nauk SSSR, Moscow, 1950, 19-82; reprinted in Ref. 15, pp 102-176. The Russian versions published earlier were translations from the German, the first by B. N. Menshutkin in D. I. Mendeleev, *Periodicheskii zakon* [*The Periodic Law*], Leningrad, 1926, 70-133; and the second by V. Ia. Kurbatov in *Works*, Vol. 25, 239-305.
38. Ref. 5, Kedrov, 1958, pp 32, 138-145.
39. Ref. 26, 1st ed., Part 1, Ch.19, reprinted in *Works*, Vol. 13, 650-652. Mendeleev argued that their compounds could be types for all the other compounds. Obviously, Gerhardt's "type theory" could be seen as influential here since Mendeleev was familiar from his student days. However, he did not mention Gerhardt and went directly to the concept of valence, for which he used the word atomnost' (atomicity).
40. Ref. 26, 1st ed., Part 2, Ch.3, reprinted in *Works*, Vol. 14, 120-121.
41. Ref. 3, p 77.
42. Ref. 5, pp 39-91. Also see my recent analysis of the process of the discovery, Ref. 7, pp 183-199.
43. D. N. Trifonov has criticized Kedrov's version on several minor points: "Versiya-2 (K istorii otkrytiia periodicheskogo zakona D. I. Mendeleevym)" ["Version 2 (Toward a History of the Discovery of the Periodic Law by D. I. Mendeleev)"], *Vopr. Istor. Estestvozn. Tekh.*, **1990**, No.2, 25-36; No. 3, 20-32. I. S. Dmitriev has recently offered an alternative version of Mendeleev's discovery; see Ref. 6.
44. Ref. 3, p 66.
45. Ref. 37, D. Mendelejeff, p 136, note. This is Paper II in Table 2.
46. It is often said that Mendeleev kept the text of *Principles* unchanged through all the subsequent editions, but with the addition of footnotes that became longer and longer. As I show in this paper, this interpretation is a misunderstanding or at least inaccurate. This may originate partly from the fact that most Western literature refers to the translations of later editions of *Principles* and partly from the rather vague description of the textbook by Leicester, Ref. 4, 1948, p 71. See, for example, Bensaude-Vincent, Ref. 8, p 8. Brooks has also written recently that Mendeleev made no substantial change in the organization of the book for these eight editions (Ref. 9, Brooks, p 307).
47. D. Mendeleev, *Osnovy Khimii* [*The Principles of Chemistry*], 5th ed., Ch. 15, 448-472.
48. The format of the fifth and subsequent editions was completely different from that of the preceding editions; i.e., this and subsequent editions were bound as a single volume, but English and French translations were issued in multiple volumes. This has given rise to the incorrect ideas about the formats of Mendeleev's textbook. The English translation appeared in two volumes: *The Principles of Chemistry* by D. Mendeléeff. Translated from the Russian (fifth edition) by George Kamensky, edited by A. J. Greenway in two volumes, Longmans, Green & Co., London and New York, 1891; Vol. I, xvi + 611 pp. & Vol. II, vi + 487 pp. Later, the sixth and seventh Russian editions were also translated into English and published in 1901 and 1905, respectively, as the second and third English editions. Each of these English editions also appeared in two volumes. The German translation was issued in one volume like the Russian edition:

Grundlagen der Chemie. Aus dem russischen übersetzt von L Jawein und A. Thillot, Verlag von C. Ricker, St.-Petersburg, [1890]-1891, [4], 1127 S. Both the fifth and the sixth editions were used for the French translation since the sixth edition appeared while the French edition was being prepared. The French translation should have been published in three volumes, but the third volume never appeared for some unknown reason: *Principes de chimie* par M. Dimitri Mendéléeff le professeur de chimie à l'Université impériale de Saint-Pétersbourg. Traduit du russe par E. Achkinasi [et] H. Carrion, avec préface de M. le professeur Armand Gautier. Vol. 1-2, Éditeur B. Tignol, Paris, 1895-1896; Vol. I, [4], iv + 585 pp. & Vol. II, [4], 499 pp.

49. D. Mendeleev, *Popytka khimicheskogo ponimaniia mirovogo efira* [*An Attempt at a Chemical Understanding of the Universal Ether*], St. Petersburg, 1903. An English translation appeared as D. Mendeléeff, *An Attempt Toward a Chemical Conception of the Ether*, trans. G. Kamensky, Longmans, Green & Co., New York, 1904. See B. Bensaude-Vincent, "L'éther, élement chimique: un essai malheureux de Mendéléev?" *Br. J. Hist. Sci.*, **1982**, *15*, 183-188.
50. Ref. 26, 1st ed., Part 2, Ch.6, reprinted in *Works*, Vol. 14, 247.
51. Bensaude-Vincent has pointed out that the logical consequence of Lavoisier's definition is the hypothesis of a primordial matter. See Ref. 8, p 12.
52. In 1969 van Spronsen claimed that there were six independent discoverers of the periodic law: A. E. B. de Chancourtois, J. A. R. Newlands, W. Odling, G. D. Hinrichs, J. L. Meyer, and D. I. Mendeleev. J. W. van Spronsen, *The Periodic System of Chemical Elements: A History of the First Hundred Years*, Elsevier, Amsterdam, 1969. On the other hand, in the 1860s, these six individuals had classified almost all the elements already discovered on the bas of the atomic weights proposed by Cannizzaro and on some relationships between different groups of elements. However, as I have argued elsewhere, there were significant differences in their scientific contents, as well as the social contexts, for the acceptance of their discoveries. See Ref. 7, pp 101-141, 239-260.
53. L. Meyer, "Die Natur der chemischen Elemente als Function ihrer Atomgewichte," *Ann. Chem. Pharm.*, **1870**, Supplementband, *7*, 354-364. Also reprinted in K. Seubert, Ed., *Das natürliche System der chemischen Elemente*, Ostwald's Klassiker No. 68, W. Engelmann, Leipzig, 1895, 9-17. For a partial translation of this paper into English, see Ref. 3, Leicester and Klickstein, pp 434-438.
54. Ref. 53, Meyer, pp 354-355.
55. Note that Meyer did not strictly and explicitly distinguish elements from simple bodies.
56. Ref. 53, Meyer, p 364.
57. L. Meyer, "Zur Systematik der anorganischen Chemie," *Ber. Dtsch. Chem. Ges.*, **1873**, *6*, 101-106.
58. See J. R. Smith, Persistence and Periodicity: A Study of Mendeleev's Contribution to the Foundation of Chemistry, Ph.D. Thesis, University of London, 1976, 516; also Ref. 8, Bensaude-Vincent, p 15.
59. "Refarat soobshcheniia 'O edinstve veshchestva v sviazi s periodicheskim zakonom'" ["Abstract of the Report 'On the Unity of Substance in Connection with the Periodic Law'"], *Zh. Russ. Khim. Obshch.*, **1886**, *18*, No. 1, sect. 1, 66-67, reprinted in Ref. 15, Kedrov, pp 438-439; D. Mendeléeff, "The Periodic Law of the Chemical Elements" (Faraday Lecture Delivered before the Fellows of the Chemical Society in the Theatre of the Royal Institution on Tuesday, June 4, 1889), *J. Chem. Soc.*, **1889**, *55*, 634-656, also in Appendix II of D. Mendeléeff, *Principles*, 3rd English ed., 1905, reprinted 1969, 494.
60. Ref. 52, van Spronsen, p 260. Van Spronsen has made the point that the rare earths were such an insurmountable difficulty for the periodic system that it could have been constructed only during the 1860s when few of them were known.

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