

MEMÓRIAS
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CLASSE DE CIÊNCIAS

TOMO XLVIII

**Celebration of the Periodic Table of the Elements
at the Academy of Sciences of Lisbon.
A Chemistry Symposium
Sublime Generalization:
Discovery of The Periodic Law**

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ACADEMIA DAS CIÊNCIAS
DE LISBOA

LISBOA • 2022

Sublime Generalization: Discovery of The Periodic Law

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Vadim Yurievich Kukushkin was born in 1956 in Leningrad (now Saint Petersburg), Russian Federation. He studied chemistry at Lensovet Technological Institute (Technical University), where he obtained his Diploma with distinction in 1979 and doctoral degree in 1982. Following two years at the industrially oriented Mekhanobr Institute (Leningrad), he joined the faculty at Saint Petersburg State University (1984). He obtained his post-habilitation DSc degree in 1992, was appointed full Professor in 1996 and became head of the Department of Physical Organic Chemistry in 2007. He is a full member of the Russian Academy of Sciences (elected 2019), foreign member of the Academy of Sciences of Lisbon (Portugal; elected 2011), member of the European Academy of Sciences (elected 2020), invited chair professor at the National Taiwan University of Science and Technology (since 2007). He is vice-president (elected 2016) of the Russian Chemical Society and the chairman (since 2012) of the Saint Petersburg branch of this society, member of the Councils of the Russian Foundation for Basic Research (2008–2016), Grant Commission of the Government of the Russian Federation (since 2012), and the Russian Science Foundation (since 2014; coordinator in chemistry since 2017). Prof. Kukushkin is a recipient of numerous prizes for his achievements in science and teaching. His research interests include platinum group metal chemistry, ligand reactivity, noncovalent interactions, organic synthesis involving metal complexes, and catalysis. He is an author of ca. 400 original papers, patents, reviews, as well as two books and a number of book chapters.

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In October 1867, Dmitrii Ivanovich Mendeleev (1834–1907) (**Photo 1** [1]; for 3D-virtual tour at The D. I. Mendeleev Museum and Archives see Ref. [2]) began teaching his year-long course in inorganic chemistry, which the thirty-three-year professor of Saint Petersburg University (**Photos 2–3**) delivered to freshmen at the Faculty of Physics and Mathematics. He would continue teaching this course every year until he left the University in 1890. During this period his teaching load averaged five hours of lectures per week.

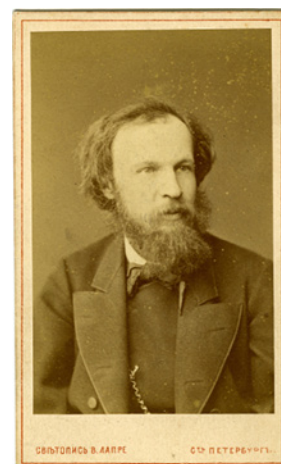


Photo 1.
Dmitrii I. Mendeleev in 1869.



Photo 2. Building of Saint Petersburg University in 19th Century (watercolor by M.B. Belyavskii).

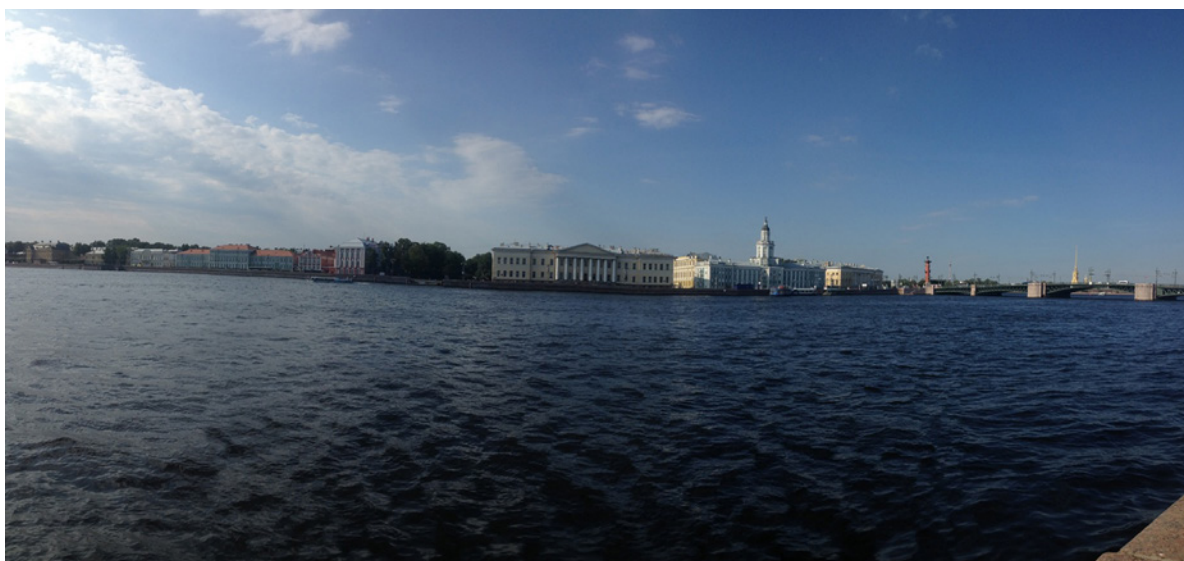


Photo 3. Panorama of Vasilyevsky Island with Saint Petersburg State University (former Saint Petersburg University) campus on the left from the park (taken 2019).

As Mendeleev himself put it, he was unable to find a textbook appropriate to such an intensive course, and thus decided to write his own, what would become the *Principles of Chemistry* (*Osnovy Khimii*). There was, however, another reason that motivated him to write the textbook. The reason was money.

Unlike a scientific monograph, a textbook can be republished many times, each time to the author's financial benefit. *Principles* became an important source of additional income for Mendeleev. Furthermore, the University granted him a sizeable cash allowance for the publication of the first issue of the textbook. For subsequent editions, as a rule, the University did not give monetary rewards (that is, only the first impulse was encouraged), but it was possible to receive royalties from the publisher. At that time, textbooks were initially published as a series of separate issues, which after making corrections and additions were later republished as a complete set, either under one cover or in several volumes.

The first issue of *Principles* appeared in the early summer of 1868. Mendeleev immediately set to work on the second issue, which was published in March 1869. These two issues made up the first part of his textbook [3]. It was during the work on the second issue of the first part of *Principles* that Mendeleev discovered the periodic law.

Notably, in the first issue of *Principles* Mendeleev did not introduce elements, atoms, or any theory of chemical combination. The issue mostly covers basic definitions, plans for chemical experiments, and general information on chemical phenomena. It is in Chapter 15 ("Carbon") of the second issue that Mendeleev first draws a clear distinction between the concepts "element" and "simple body". It was a historical turning point leading up to the discovery of the periodic law. Before turning to classification, one must understand what is there to classify.

Mendeleev understood that it were not simple bodies that had to be classified, but chemical elements. The concept of an element corresponded to the smallest chemically indivisible weight amount of matter of a certain type entering the particles (molecules) of bodies. Thus, an element in the understanding of Mendeleev was an "abstract concept", "matter contained in a simple body and capable of passing into all bodies resulting from this body without a change in weight." An element, according to Mendeleev, potentially contains in itself all the possible forms, properties and states that it is able to reveal under certain conditions. The possibility (or impossibility) of the formation of certain compounds, allotropic modifications, metallic or other states, etc., is all included (encapsulated) in the concept of "element". In other words, a simple body turns out to be, in the language of Aristotle, the *entelechy* of the element, that is, the realization of what existed potentially (Phys. III.1; Metaph. IX.8) in the chemical element.

Mendeleev's first article on the periodic law began with the following words: "The systematic distribution of elements has been subjected in our science to various vicissitudes". This was true. But Mendeleev kept silent about one thing: the problem of the "systematic distribution of elements" for the contemporary scientific community was considered utterly marginal, not worthy of attention for a serious scientist. Mendeleev decided to develop his system of classification of elements in spite of this widespread derision.

The most active phase of his work on the first two issues of his textbook and the classification of elements fell on 1867–1869. Mendeleev split the workload between his estate in Boblovo (Tver' province) and his University-owned apartment in Saint Petersburg (**Photo 4**, left). Since he suffered from



Photo 4.

Left: Mendeleev's home office; right: the bureau at which Mendeleev worked.

hemorrhoids, he often had to work while standing at the bureau (**Photo 4**, right). It was while working at this desk that he discovered the periodic law.

“FIRST ATTEMPT”

We will begin with the testimony of Mendeleev himself: “The first attempt made in this respect was the following: I selected the bodies with the lowest atomic weights and arranged them in order of magnitude of their atomic weight. It turned out that there exists a sort of periodical repetition of properties of simple bodies, and even in atomicities (valencies) elements follow each other in the order of the arithmetic sequence of the magnitude of their atomic weights:

Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19
Na = 23	Mg = 24	Al = 27.4	Si = 28	P = 31	S = 32	Cl = 35.5
K = 39	Ca = 40	–	Ti = 50	V = 51	→	

... The following suggestion immediately springs to mind: perhaps the properties of the elements are displayed in their atomic weights, and could one then base a system on these?” [4; page 17].

Already when considering these light elements (with atomic weights from 1 to 40), Mendeleev arrived at important assumptions:

1. “Are the properties of elements in their atomic weight expressed, is it possible to create the system on it?” [4; page 18];

2. When the elements are ordered by their atomic weights, a “sort of period of properties” is observed. Thus, even if Mendeleev had not yet proposed the final formulation of the periodic law, he had already grasped its essence, the main point – the periodic nature of change in the properties of elements following the increase in their atomic weights. All his further efforts were aimed at testing this proposition, which at that point remained merely a hypothesis. The word “hypothesis” is, however, missing in the text of his first article on the classification of chemical elements. Instead, Mendeleev uses the word “law”:

“I propose that the law (*zakon*) I have established does not contradict the general direction of the natural sciences, and that until now its proof has not appeared, although there were already hints of it. From now on, it seems to me, a new interest will develop in the determination of atomic weights, in the discovery of new simple substances, and in the seeking out of new analogies between them” [4; page 21].

However, what exactly Mendeleev called “law” requires a more specific definition, and we will return to this further.

3. It is possible to build a system of elements from structural units of the following form:

Alkali Metals –	Intermediate Elements – “exhibiting less expressed chemical character” [4; page 22]	Halogens
		(1)

By “chemical character” Mendeleev meant all properties of a simple body corresponding to a given element. Elements “exhibiting less expressed chemical character” comprised those with less pronounced “metallic” character than the alkali metals but less “non-metallic” than the halogens.

In other words, Mendeleev decided to build a system of elements by stacking fragments of type (1) in such a way that the atomic weights increase from top to bottom and from left to right.

This was a powerful insight, but Mendeleev’s design was not easy to implement due to a number of difficulties:

- not all elements were known at that time (1869);
- for known elements, not all atomic weights were correctly defined, and it remained unclear which ones were to be trusted;
- the number of elements in different parts of type (1) was unequal: there were only five elements between Li and F, as well as between Na and Cl, while the interval between K = 39 and Br = 80 had to accommodate at least 12 elements known at the time: Ca = 40; Ti = 50; V = 51; Cr = 52; Mn = 55; Fe = 56; Co = Ni = 58.8; Cu = 63; Zn = 65; As = 75; Se = 79):

Li	Be	B	C	N	O	F													
Na	Mg	Al	Si	P	S	Cl													
K	Ca	–	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	–	–	As	Se	Br			
Rb	Sr	–	Zr	Nb	Mo	–	Rh	Ru	Pd	Ag	Cd	U	Sn	Sb	Te	I			

- the intervals (Li–F) and (Na–Cl) differed from the rest not only in the number of elements contained in them, but also, and more importantly, in their chemical character, as well as in the rate and

rhythm of changes in the properties of simple bodies and corresponding compounds when moving from an alkali metal to halogen (for example, such elements as V, Cr, Mn, whose chemistry was significantly different from the chemistry of direct analogues of phosphorus, sulfur, and chlorine, i.e. As, Se, and Br, turned out to be among the K–Br series);

- there were two types of analogies between elements, which had to be somehow reflected in the system. This last difficulty should be considered in more detail.

Variant (2) did not suit Mendeleev, and it is easy to see why. In the first two lines, the analogous elements are located underneath one another, highlighting their natural order. In the third line however, As, a direct analogue of phosphorus, Se, a direct analogue of sulfur, and Br, a direct analogue of chlorine, were pushed to the side, sidestepped by other elements. Mendeleev decided “to break” the long lines:

Li	Be	B	C	N	O	F			
Na	Mg	Al	Si	P	S	Cl			
K	Ca	–	Ti	V	Cr	Mn	Fe	Co	Ni
Cu	Zn	–	–	As	Se	Br			
Rb	Sr	–	Zr	Nb	Mo	–	Rh	Ru	Pd
Ag	Cd	U	Sn	Sb	Te	I			

(3)

This, however, did not resolve the difficulties. Some elements (for example, Fe, Co, Ni) ended up “suspended” outside the system. Worse yet, although arsenic was brought to same column with phosphorus, selenium with sulfur and bromine with chlorine, in these columns the elements that were direct analogues were blended with “aliens”: between phosphorus and arsenic appeared vanadium, between sulfur and selenium – chromium, between chlorine, and bromine manganese... Was there anything in common between vanadium and phosphorus? At first glance, the two elements seemed nothing alike. But only at first glance. And Mendeleev knew that.

“SOME DIFFICULTY”

He knew that vanadium and phosphorus (as well as chromium and sulfur, or chlorine and manganese) were not entirely “alien” to each other. There was some similarity between them, but it manifested itself only in higher compounds. For example, the highest degree of oxidation of both chlorine and manganese is 7 (later they will be in the seventh group), and the corresponding higher compounds of these elements (Cl_2O_7 and Mn_2O_7 ; KClO_4 and KMnO_4 etc.) exhibit similar properties. The same can be said about the P–V and S–Cr pairs.

Mendeleev was aware of this prior to 1869, as were many other chemists before him, but the question remained: was this similarity of higher compounds, say, higher oxygen compounds, due to the similarity of the elements themselves, which were in a special, “limiting” state, or due to there being so much oxygen in these compounds that it equalized (“camouflaged”) differences in the nature of the

generic elements? This was one of the hardest questions facing Mendeleev, and it took him a long time, at least a year, to answer it.

Thus, the variant (3) of the system of elements, which quite satisfied such predecessors of Mendeleev as William Odling and Lothar Meyer, and which suits us today, to Mendeleev in early 1869 was completely unacceptable. The main reason he rejected this variant was the lack of clear and strict criteria for incorporating into one column elements of different classes (*razryad*), as they were then called, or, in modern terminology, the main-group (i.e. *ns*- and *np*-elements) and transition elements (i.e. $(n - 1)$ *d*-elements).

With the criteria for unifying the elements of both “classes” into one group not yet clear, although even in his first article on the periodic law Mendeleev already wrote that, for example, “in manganese there is some similarity with chlorine, as in chrome with sulfur” [4; page 26]. Mendeleev was having “some difficulty”, as he carefully put it later [5; page 78]. And besides that such “difficulty” arose at all, Mendeleev must have had at his disposal such a form (or structure) of a system of elements that would become the source of said difficulty. Such a form could only be a system of type (3). But in the absence of criteria for unifying dissimilar elements into one group, he could not use this form of the table, so it seemed to him more natural to separate elements of different classes.

That was his decision. In this way, after closely approaching the variant of the system that would later be known as the “short form: (or “natural system”), Mendeleev refused to place transitional elements among the elements of the main subgroups, arguing that should manganese be positioned in the column between chlorine and bromine, chromium between sulfur and selenium, vanadium between phosphorus and arsenic, etc., “the naturalness of the relations of members of the same... row [i.e., members of the same main subgroup, as we would say today. – I. S. D., V. Yu. K.] would be broken” [4; page 26].

The task of unifying elements of different “classes”, set by Mendeleev, may seem relatively simple, but only at first glance. After all, one had to precisely regroup more than sixty elements, to do so in such a way so as to keep their arrangement by increasing their atomic weights, and in no way obscure the periodic nature of changes in the properties of elements. Otherwise, the system lost its integrity and value. The task was complicated by the fact that Mendeleev initially attributed Cu, Ag, Zn and Cd to the elements of the first class, i.e. to the elements of the main subgroups, in modern terms.

Since the short form of the system (with “broken” periods) did not seem to fit, Mendeleev tried his luck with another form that would later become the “long” (or “long-period”) version:

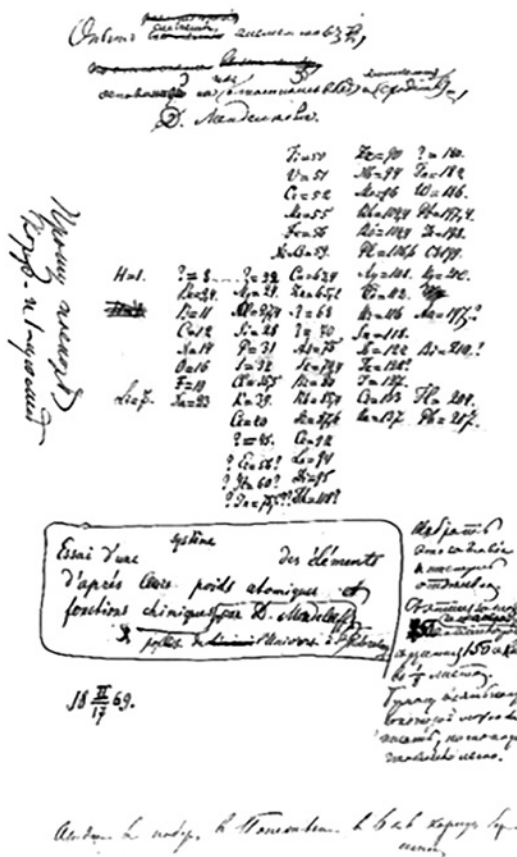
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	–	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	–	–	As	Se	Br
etc.																

Alas, this allocation of elements did not satisfy Mendeleev either, since he was confused by the emptiness (gaps) in the first two lines. The empty space inside the natural system seemed to suggest the existence of elements not yet discovered, whereas there was no reason to suspect the existence of unknown elements between Be and B and between Mg and Al.



Photo 6. Nikolay A. Menshutkin (1842–1907), Secretary of the Russian Chemical Society and editor of *The Journal of the Russian Chemical Society*. Mendeleev handed “Attempted System” over to him for publication in the *Journal* and for communication at the upcoming meeting of the society. Menshutkin fulfilled Mendeleev’s request and on March 6th, 1869 made on his behalf a presentation on the periodic law. Thus, Mendeleev found an optimal way to publicize his work, i. e., through a communication by Menshutkin, the editor of the *Journal*, on behalf of the author of the forthcoming publication, thus avoiding the risk of excessive polemics. Meanwhile, Mendeleev went on March 1st, 1869, to Tver Governorate, where he planned to inspect artel (i. e., cooperative) cheese factories [6; page 105]. The works of Menshutkin were primarily focused on studies of the kinetics of chemical transformations of organic compounds. While studying the decomposition of tertiary amyl acetate upon heating, Menshutkin observed (1882) that one of the reaction products (acetic acid) accelerates the process; this is now a classic example of auto-catalysis. He also discovered the effect of solvent on kinetics (1887–1890), as well as the effect of dilution and chemical structure on the rate of a reaction. In 1890, he discovered the alkylation reaction of tertiary amines by alkyl halides to give quaternary ammonium salts (the Menshutkin reaction).

As a result, Mendeleev, surmounting many obstacles, created a version of the system that he called with uncharacteristic modesty “An Attempt at a System of Elements, Based on Their Atomic Weight and Chemical Affinity” (hereinafter abbreviated as “Attempt”). The handwritten leaflet with the “Attempt” (**Photo 5**) is dated by hand: February 17th, 1869 (hereinafter all dates are given according to the Julian Calendar). The first public announcement of the discovery of the periodic law was made by Nikolai Menshutkin, a friend of Mendeleev (**Photo 6**).



“TWO LAWS OF DMITRY MENDELEEV”

Let us now return to a question raised above regarding the word “law”. As noted by Michael Gordin [7; page 31], and before him by Stefan Zamecki [8; page 124]. Mendeleev’s “law” refers not to a periodic dependence of properties of elements on their increasing atomic weight, but to a completely different statement, namely: “All the comparisons which I made in this direction bring me to the conclusion that the magnitude of atomic weight determines the nature of the element.” [4; page 21]. But this is not at all a statement of the periodic law. Moreover, in an article published in August 1869 on the

Photo 5. Final manuscript of “An Attempt at a System of Elements” (February 17th, 1869).

variation of atomic volumes over the periodic system, Mendeleev shied away from the word “law” and called it a “regularity (*pravil'nost'*)”. According to Gordin, only “by November 1870, [Mendeleev] was utterly convinced of both the “naturalness” and the law-like character of his periodic law [7; page 31].” Neither Gordin, nor Zamecki went beyond mentioning this interesting fact. It does, however, point to an important feature in the development of Mendeleev’s ideas regarding the classification of elements. On February 17th, 1869 (or, more precisely, by this day) Mendeleev discovered not one, but two laws. The first law was that the atomic weight of elements determines their properties; the second specified the nature of the change in the properties of elements as their atomic weights increased. The discovery of the first law was a logical consequence of Mendeleev’s ideas about the effect of body weight on its physical and chemical properties. Chemical phenomena, Mendeleev emphasized, following in the footsteps of Claude Louis Berthollet, are determined not only by the quantity of chemical energy (the strength of chemical affinity), but also by the mass of interacting bodies [9]. If one considers this idea at the atomic level, it can be said that the atom of a given element is characterized not only by a certain amount of chemical energy, but also by a certain mass (weight); and the chemical energy of the atom (and therefore its properties) depend on the atomic mass (weight):

Chemical energy of the atom = f(A), where A is the atomic weight.

Mendeleev had no fundamental difficulties with this direction of ideas, and therefore the assertion that “atomic weight determines the properties of an element” he described as a law of nature. With the second law, the law of periodicity, everything was different. Due to the unresolved problem of unifying elements of different classes, Mendeleev preferred to describe the phenomenon he discovered not as a “law”, but as “regularity”.

Academician Nikolay N. Zinin and Adjunct Aleksander M. Butlerov at a meeting on November 24th, 1870, of the Physics and Mathematics Department of the Saint Petersburg Academy of Sciences presented the Mendeleev’s article “On the Place of Cerium in the System of Elements”. In that paper, Mendeleev gives a table entitled simply and briefly – “System of elements”, which became the prototype of the short form of the system known today, and which Mendeleev called in another article “The Natural System of Chemical Elements” (1870) [5] (**Photo 7**).

Although Mendeleev worked on it concurrently with the article “On the Place of Cerium...” (**Photo 8**), the graphic expression of the periodic law presented in the “Natural System” was substantially improved from the initial version. It was included by Mendeleev in the second part of the first edition of the “Principles of Chemistry” (1871), and the name of the author was indicated in the title: “The Natural System of Elements of D. Mendeleev” (**Photos 9–10**).

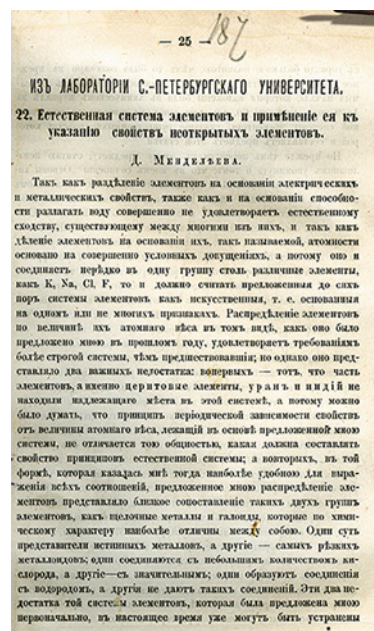


Photo 7.

The first page of the article by Mendeleev “A Natural System of the Chemical Elements” (November 29th, 1870) [5] with a detailed elaboration on the essence of the periodic law. Regarding this article, Mendeleev wrote that he decided to publish it “in order to establish the periodicity of the elements. It was a risk but the right (and successful) one” [10; page 54].



Photo 8.

D. Mendeleev at his office at The Chamber of Weights and Measures, Saint Petersburg (1904).

ЕСТЕСТВЕННАЯ СИСТЕМА ЭЛЕМЕНТОВЪ Д. МЕНДЕЛѢЕВА.

Photo 9. Natural system of the elements of D. Mendeleev (November 1870) from his textbook “Principles of Chemistry” (1st edition, part 2; 1871).

Photo 10. World’s oldest periodic table displayed at the lecture theater of the Mendeleev Center of Saint Petersburg State University. Left panel: “D.I. Mendeleev’s Periodic Law, 1869”; right panel: “The Table Made as Directed by the Author in 1878.”

REFERENCES AND NOTES

- [1] The originals of photographs 1–2 and 5–9 belong to the open collection of D. Mendeleev Museum and Archives (Saint Petersburg State University) and their copies were made by I. S. Dmitriev. Photographs 3–4 were taken by V. Yu. Kukushkin and I. S. Dmitriev, respectively, and they comprise parts of their private photo collections.
- [2] Virtual 3D-tour at The D. I. Mendeleev Museum and Archives: <https://english.spbu.ru/images/vtour/mendeleev/index.html>
- [3] D. I. Mendeleev, Principles of Chemistry [1st Edition]. SPb.: “Obshchestvennaya pol’za”. Part I, Issue 1 (1868), IV, 400 p.; Issue 2 (1869), pp. 401–816; Part II, Issue 3 (1870), 392 p.; issues 4/5 (1871), pp. 393–952.
- [4] (a) D. Mendeleev, Sootnoshenie svoystv s atomnym vesom elementov [On the Relationship of the Properties of the Elements to Their Atomic Weights]; (b) D. Mendeleev. Periodicheskii zakon. Osnovnyye stat’i [Periodic Law. Basic Papers], Ed. B. M. Kedrov. Moscow: Izdatelstvo AN SSSR, 1958, pp. 10–31 and p. 18. Original: Zhurnal Russkogo Khimicheskogo Obshchestva [Journal of the Russian Chemical Society], 1869, 1, 60–79.

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- [6] I. S. Dmitriev, Chelovek Epokhi Peremen (Ocherki o D. I. Mendeleeeve i ego Vremeni) [Man of the Time of Change (Essays on D. I. Mendeleev and his Epoch)]. Saint Petersburg: Khimizdat, 2004; 576 pp. [in Russian].
- [7] M. D. Gordin, A Well-Ordered Thing: Dmitrii Mendeleev and the Shadow of the Periodic Table. New York: Basic Book, 2004, 518 pp.
- [8] S. Zamecki, Mendeleev's First Periodic Table in its Methodological Aspect, *Organon*, **1995**, 25, 105–126 (p. 124).
- [9] Notably in the *Principles of Chemistry*, Mendeleev puts a strong emphasis on the views of Berthollet, and specifically on the description of the so-called Indefinite Compounds such as solutions, alloys, isomorphous mixtures, and silicate compounds. At that time, in the 1860s, these views went against prevailing traditions (as noted by P. Grapí and M. Izquierdo, "The textbook tradition... contributed to marginalize Berthollet's system" in P. Grapí and M. Izquierdo, Berthollet's Concept of a Chemical Change in Context, *Ambix*, **1997**, 44, 113–130 (p. 119)).
- [10] Arkhiv D. I. Mendeleeva. T. 1. Avtobiograficheskie materialy. Sbornik dokumentov / Sost. M. D. Mendeleeva i T. S. Kudryavceva. Pod obshchey red. S. A. Shchukareva i S. N. Valka. [The Archive of D. I. Mendeleev. T. 1. Autobiographical Materials. Collection of Documents / Compilation by M. D. Mendeleeva and T. S. Kudryavtseva. Ed. S. A. Schukareva and S. N. Valka] Leningrad: Izdatel'stvo Leningradskogo Universiteta