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History of the Periodic System of the Elements

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ABSTRACT

There were several attempts to classify known elements before Mendeleev. Numerous scientists, such as John Newlands, Alexandre-Emile Beguyer de Chancourtois and Julius Lothar Mayer, have contributed to the discovery of the periodic table.
Mendeleev was not the first to try to arrange the elements according to their properties, but he was the first to recognize and leave empty positions for the elements to be discovered. Many of his predictions came true and time confirmed the periodic law and the accuracy of the periodic table of elements.

Keywords: Periodic Table, Mendeleev, history, standard form, alternative form

Introduction

What is the quality of a great scientist? When we hear anecdotes about scientists who have dealt with important scientific issues, they often seem harmonious, peaceful, and interesting. However, in themselves there is a period of struggle and confusion that ends when alone genius sees the light, perhaps in a dream. Then everything falls into place, the paradigm changes and nothing is the same anymore. That, however, sounds more noble than the stories of numerous desperate attempts to solve a scientific problem, right? (Philip Ball, 2019)

Great scientists discover new facts, find meaning in it and connect it with other already known facts and resolve important issues. They also give their explanations, which other scientists accept as correct, although sometimes not immediately. Nevertheless, a good scientist goes further and predicts the consequences of his ideas that can be tested. This courage is a characteristic of great scientists. One of them was a Russian chemist Dmitry Mendeleev - the creator of the Periodic Table of the Elements.
He was not the first to try to arrange the elements according to their properties, but he was the first to recognize and leave gaps that must match elements that have not yet been discovered. Many of his predictions came true and thus strengthened his legacy (Joshua Howgego, 2021).

Others, such as John Newlands, Alexandre-Emile Beguyer de Chancourtois and Julius Lothar Meyer, contributed to the first Periodic Table of the Elements, but the greatest contribution goes to Mendeleev.

Historical development

Chemists studied each chemical element separately. Connection between them was observed, although some were very similar to each other, and some were quite different in physical and chemical properties. They could not even guess how many elements there are. It was a real question which property of the elements to take as a criterion in their classification (Mandić et al., 2011).

Chemists have always searched ways to arrange the elements according to their properties. The formation of the Periodic Table is something that is routinely attributed to Mendeleev; however, the periodization and systematization of the elements has a much longer history. Certainly, Mendeleev was the first to publish the version of the system that we accept today, but do all the merits belong to him? Other chemists before Mendeleev also studied the properties of elements that were known at their time, searching for appropriate patterns. As in many other scientific discoveries, other scientists have come close to the same.

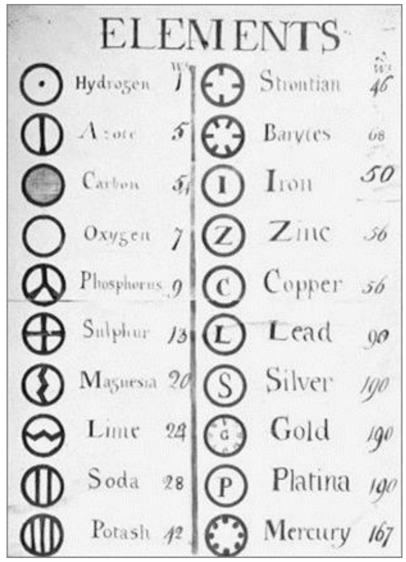


Figure 1. Dalton’s symbols (Stack Exchange Inc., 2021).

Although the structure of the atom was not known at that time, the idea of the modern Periodic Table was well established and used to predict the properties of undiscovered elements long before the concept of atomic number was developed (Royal Society of Chemistry, 2021).

As early as the 17th century, more precisely in 1661, Robert Boyle ranked 13 known elements by increasing relative atomic masses. During the 18th century, some new elements were discovered and marked with geometric, astronomy and astrology symbols (Figure 1).

This system was expanded by Antoine-Laurent de Lavoisier with 11 elements. In 1789, Lavoisier made the first modern list of elements-33 of them, including light, warm, unextracted radicals and some oxides. He grouped them based on their properties into gases, not metals, metals and earths (Figure 2) (Royal Society of Chemistry, 2021).

	Noms nouveaux.	*Noms anciens correſpondans.*
Subſtances ſimples qui appartiennent aux trois règnes, & qu'on peut regarder comme les élémens des corps.	Lumière	Lumière.
	Calorique	Chaleur.
		Principe de la chaleur.
		Fluide igné.
		Feu.
		Matière du feu & de la chaleur.
	Oxygène	Air déphlogiſtiqué.
		Air empiréal.
		Air vital.
		Baſe de l'air vital.
	Azote	Gaz phlogiſtiqué.
		Mofète.
		Baſe de la mofète.
	Hydrogène	Gaz inflammable.
		Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre	Soufre.
	Phoſphore	Phoſphore.
	Carbone	Charbon pur.
	Radical muriatique	Inconnu.
	Radical fluorique	Inconnu.
	Radical boracique	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine	Antimoine.
	Argent	Argent.
	Arſenic	Arſenic.
	Biſmuth	Biſmuth.
	Cobalt	Cobalt.
	Cuivre	Cuivre.
	Etain	Etain.
	Fer	Fer.
	Manganèſe	Manganèſe.
	Mercure	Mercure.
	Molybdène	Molybdène.
	Nickel	Nickel.
	Or	Or.
	Platine	Platine.
	Plomb	Plomb.
	Tungſtène	Tungſtène.
	Zinc	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux	Terre calcaire, chaux.
	Magnéſie	Magnéſie, baſe du ſel d'epſom.
	Baryte	Barote, terre peſante.
	Alumine	Argile, terre de l'alun, baſe de l'alun.
	Silice	Terre ſiliceuſe, terre vitrifiable.

Figure 2. Lavoisier's periodic system (HolidayMapQ.com, 2020)

He also redefined the term chemical element. It was found that water is made of hydrogen and oxygen, air of oxygen and nitrogen, so they realized that water and air cannot be elements. He, therefore, concluded that substances that decompose into simpler ingredients are not elements (Anonymous, 2014-2020). By then, any metal except mercury was not considered element. Lavoisier helped to build the metric system, wrote the first list of elements, and established the basis of chemical nomenclature. He predicted the existence of silicon (1787) and he established sulfur as an element (1777) and not a compound. He found that although matter can change shape or state, its mass always remains the same — the Law of Conservation of Mass (Anonymous, 2014-2020).

Through the entire XX century there was a search for a more precise classification scheme. During this period, significant discoveries in the field of chemistry and physics enabled the discovery of new elements. This was the reason to classify the growing number of known elements.

In 1803, John Dalton proposed his principles of atomic theory (he introduced the concept of atomic weight or, more precisely, relative mass, taking the hydrogen atom as the standard, because it is the lightest and attributed atomic mass to it 1), suggesting that all elements composed of tiny, indestructible particles, called atoms. Atoms of the same element are equal and have the same mass. Atoms of an element can enter or leave new molecules during a chemical reaction, but their total mass remains unchanged (Wikipedia, John Dalton, 2021).

The first common chemical characteristics of the elements were noticed by the German chemist Johann Wolfgang Döbereiner. In 1829, he noticed that the properties of bromine lay somewhere in between the properties of chlorine and iodine. The same could be applied to the following three elements: calcium, strontium, barium as well as sulfur, selenium and tellurium. Lithium, sodium, and potassium, for example, are grouped together in a trinity as soft reactive metals, and it has been shown that the properties of the middle element can be predicted from the properties of the other two. Since the elements are gathered into groups of three elements, this Döbereiner's classification attempt is called the Law of Triads (Figure 3). This was certainly a good start, but Döbereiner abandoned his idea so it was understood only as a mere coincidence and was quickly forgotten (Kepić, 2013).

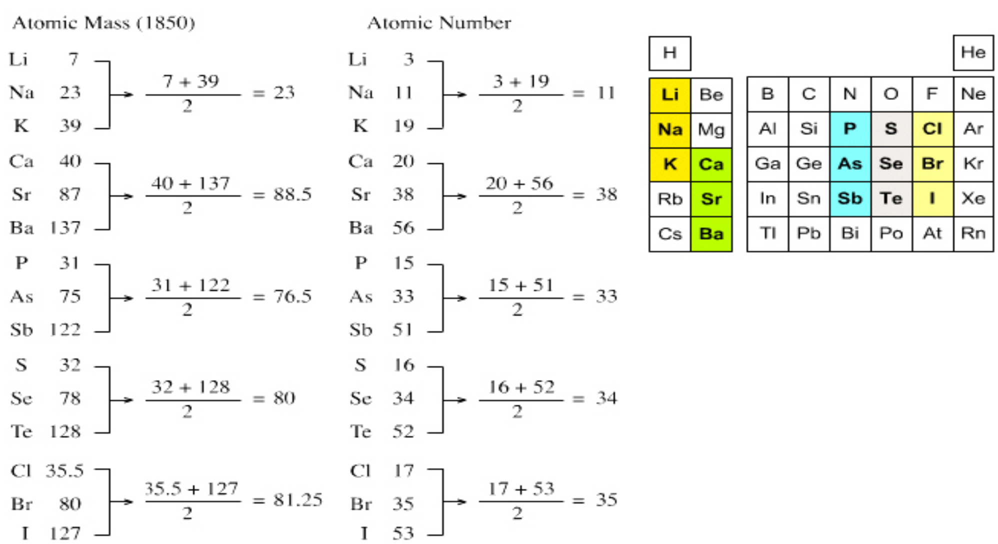


Figure 3. Döbereiner's periodic system (hemija.biologijakp.com, 2021)

The German chemist, Leopold Gmelin was using the mentioned law in his work and by 1843 he had identified ten trinities, three groups of four elements, and one group of five elements (Figure 4) (Wikipedia, Leopold Gmelin, 2019).

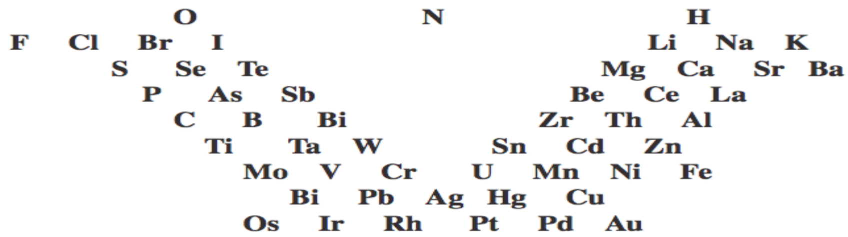


Figure 4. Gmelin's periodic system

(The Chemogenesis Web Book, The Internet database of periodic tables, 2021)

In 1857, Jean-Baptiste Dumas published a paper in which he described the relations between different groups of metals. Although many chemists were able to identify relationships between small groups of elements, it was still necessary to create a single scheme that would include all the elements (Wikipedia, Jean-Baptiste Dumas, 2021).

The German chemist August Kekulé, observing carbon, realized that this element usually has four other atoms attached to it. Methane, for example, has one carbon atom and four hydrogen atoms. This concept eventually became known as a valence; different elements bind to different numbers of atoms (Wikipedia, August Kekule, 2021).

The first attempt of chemical periodicity was announced by the French geologist Alexandre-Emile Beguyer de Chancourtois. In 1862, he published the first three-dimensional forms of the Periodic Table and called it a telluric helix. De Chancourtois was the first scientist who noticed the periodicity of the elements. He showed that elements with similar properties mostly appear at regular intervals, by arranging the elements spirally on the cylinder, according to the increasing atomic weight. His diagram also contained some ions and compounds in addition to the elements. This work did not rise much interest (Wikipedia, Alexandre-Emile Beguyer de Chancourtois, 2020).

In the United States, the Danish emigrant, Gustavus Detlef Hinrichs, also realized that all elements could be included within a single coherent system, as did the German chemist Lothar Meyer.

Gustavus Detlef Hinrichs, in 1867, published a spiral periodic system based on atomic spectra, weights, and chemical similarities. His work was characterized as "idiosyncratic, ostentatious and labyrinthine", which negatively contributed to the recognition and acceptance of the same (Wikipedia, Gustavus Detlef Hinrichs, 2020).

Julius Lothar Meyer, a German chemist, in 1864 published a periodic table with 44 elements arranged according to valence (Wikipedia, Lothar Meyer, 2020).

The table shows that elements with similar properties usually have the same valence. Meyer never came up with the idea to predict the discovery of new elements and to correct atomic masses. Just a few months after Mendeleev's system, Meyer released a virtually identical system. Some people consider Mendeleev and Meyer to be the co-creators of the Periodical System (Opusteno.rs, 2016).

This was followed by the discoveries of two London chemists, John Newlands and William Odling, who came to their basic periodic systems while working completely independently.

Certainly, the most serious move towards today's Periodic Table, before Mendeleev, was given by John Newlands, an English chemist, who made a series of projects in the period from 1863 to 1866. He discovered that when elements are arranged according to the increasing value of their atomic weights, similar physical and chemical properties begin to be repeated in the interval number eight. He compared this periodicity to octaves in music and called it the Law of Octaves (Wikipedia, John Newlands (chemist), 2020). If you have one proton, it is hydrogen. If you have 12 protons, that’s carbon. As you add protons, you will find that similar properties appear after every 8 elements. Lithium, for example, with atomic number 3, is a reactive metal - just like sodium (element number 11) and potassium (number 19) (Figure 5). A good way is to imagine running your fingers over the piano keys. The notes resonate at higher and higher pitches as the hand moves to the right. By pressing the eighth key, something beautiful happens - a note is heard in the air that has something from the first one. As a sign of respect for this musical analogy, this law justified its name (Joshua Howgego, 2021). In vertical columns, the elements were arranged in ascending order of atomic relative mass, while horizontal species were conditioned by similarity in properties. Newlands was too consistent in arranging the elements by increasing atomic mass and he overlooked the fact that many elements had not yet been discovered, so his table had many shortcomings (Kepić, 2013). This so-called Octave Law, however, was ridiculed by most Newlands’ contemporaries, and the Chemical Society refused to publish his work, noting that it would certainly find some legitimacy if he arranged the elements in the alphabetical order. Despite this, Newlands managed to create a system of elements and use it to predict the existence of missing elements, as is the case with germanium. The Chemical Society acknowledged the importance of his discoveries only five years after the credit went to Mendeleev (Wikipedia, John Newlands (chemist), 2020).

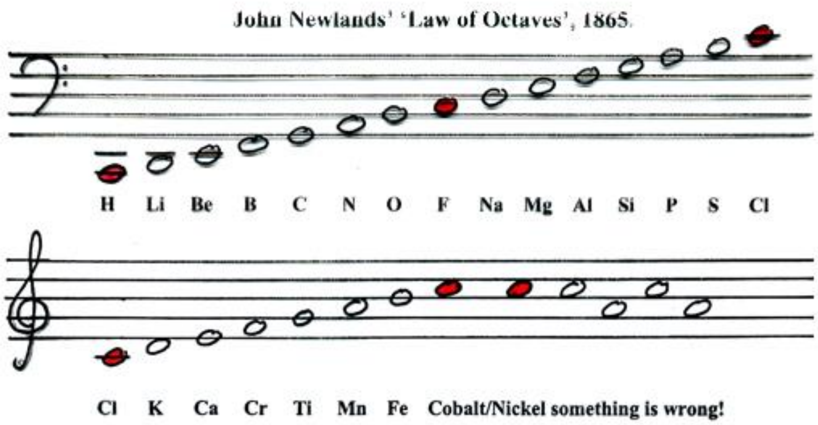
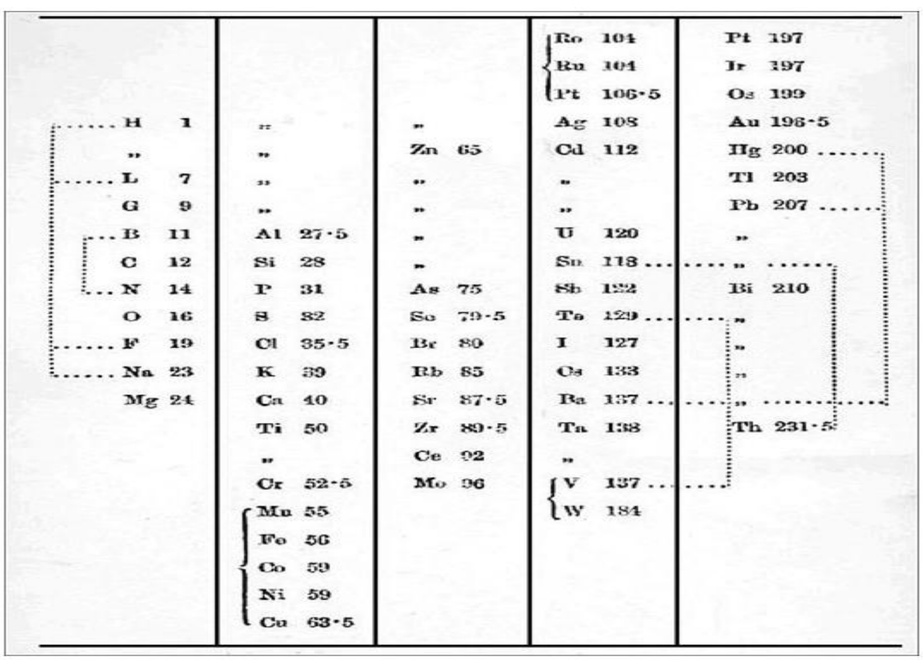


Figure 5. Newlands' periodic table (SlidePlayer.com Inc., 2021)

William Odling, an English chemist, published his system with 57 elements arranged according to their atomic weights. With a few irregularities and omissions, he noticed among the elements something resembling the periodicity of atomic weights and this was consistent with "their mostly acquired groupings" (Figure 6). Odling was close to the discovery of the periodic law, but he failed to conduct the research to the end. Subsequently, in 1870, he proposed the classification of elements based on their valence (Wikipedia, William Odling, 2020).



			Ro 104	Pt 197
			Ru 104	Ir 197
			Pt 106·5	Os 199
H 1	"	"	Ag 108	Au 196·5
"	"	Zn 65	Cd 112	Hg 200
L 7	"	"	"	Tl 203
G 9	"	"	"	Pb 207
B 11	Al 27·5	"	U 120	"
C 12	Si 28	"	Sn 118	"
N 14	P 31	As 75	Sb 122	Bi 210
O 16	S 32	Se 79·5	Te 129	"
F 19	Cl 35·5	Br 80	I 127	"
Na 23	K 39	Rb 85	Cs 133	"
Mg 24	Ca 40	Sr 87·5	Ba 137	"
	Ti 50	Zr 89·5	Ta 138	Th 231·5
	"	Ce 92	"	
	Cr 52·5	Mo 96	V 137	
	Mn 55		W 184	
	Fe 56			
	Co 59			
	Ni 59			
	Cu 63·5			

Figure 6. Odling's periodic table

(The Chemogenesis Web Book, Odling's table of elements, 2021**)**

None of these scientists was able to predict new elements that could be discovered, or to emphasize the value of the Periodic Table, as Mendeleev did.

Year of discovery (1869)

All these ideas, however, remained in the field of experimentation and were only an overture to following discoveries (Kepić, 2013).

The first "mosaic" that contained all 63 elements known until then, was assembled by the Russian chemist Dmitri Ivanovich Mendeleev. In 1869, he made the Periodic Table of chemical elements as a graphical representation of the periodic law. According to that law, the properties of elements are periodically repeated, because they depend on their atomic masses. He attributed the connection between the elements to their atomic masses (Mandić et al., 2011).

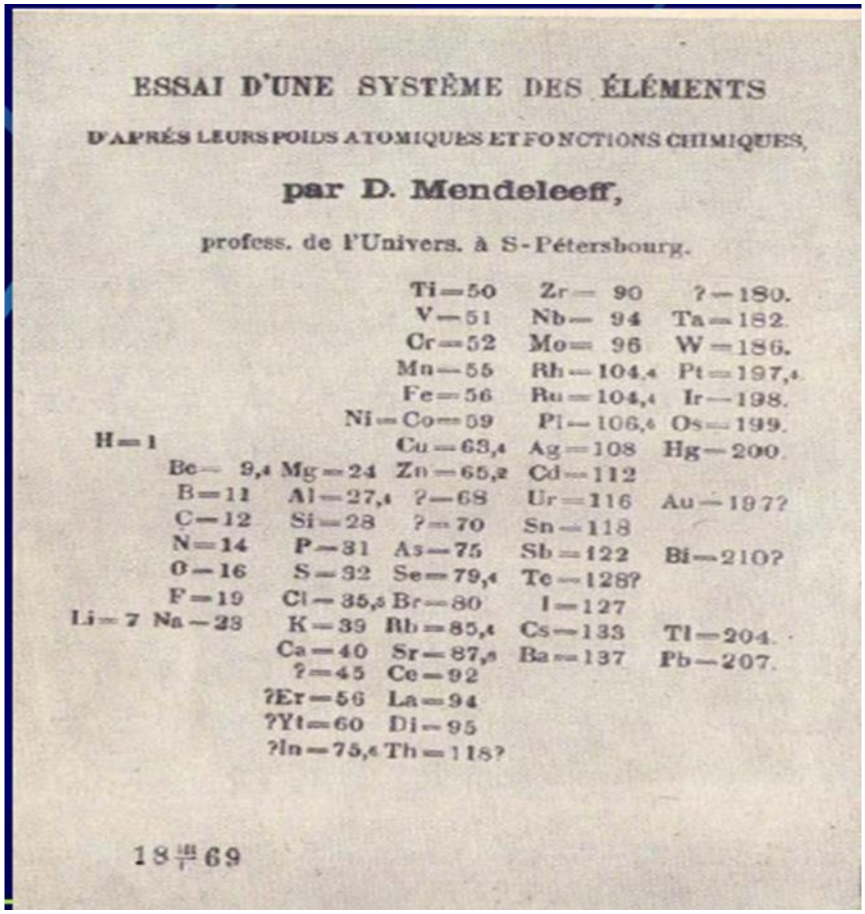
Mendeleev realized that there were not enough quality books on chemistry and decided to write a book on his own, a capital book for that time: Principles of Chemistry in Two Volumes (1868-1870). While writing this book, he came to the discovery that was his greatest achievement (Edukacija, 2014-2020). He tried to classify chemical elements according to their chemical properties, which he observed in regular repetitive patterns, which led him to compile his Periodic Table (Wikipedija, Dmitrij Mendeljejev, 2021). Mendeleev gradually formed a file, where each chemical element known until then had its own card with the name, basic properties, and the most important compounds. Comparing the cards, Dmitry Ivanovich noticed regularities. When he placed the chemical elements in order of increasing relative atomic masses, he saw that they periodically repeated the chemical properties (Antonijević Ivana, 2013). He made the following table (Table 1):

Table 1. Mendeleev's cards with elements

Cl 25.5	K 39	About 40
Br 80	Rb 85	We 88
I 127	Cs 133	Ba 137

In creating the Periodic Table, he strictly adhered to the periodic repetition of these properties and at the cost of minor deviations from the order of the elements as the atomic mass increased, which shows that he intuitively understood the essence. By adding other elements and following this scheme, Dmitri developed an expanded version of his Periodic Table (Antonijević Ivana, 2013).

All the elements known until then found their place in the table, and those that were subsequently discovered were placed in the empty spaces left for them. Mendeleev then classified known elements according to a similar principle as Newlands, he placed related elements one below the other (Kepić, 2013).


ESSAI D'UNE SYSTÈME DES ÉLÉMENTS
D'APRÈS LEURS POIDS ATOMIQUES ET FONCTIONS CHIMIQUES,
par D. Mendeleeff,
profess. de l'Univers. à S-Pétersbourg.

			Ti=50	Zr=90	?=180.	
			V=51	Nb=94	Ta=182.	
			Cr=52	Mo=96	W=186.	
			Mn=55	Rh=104,4	Pt=197,4.	
			Fe=56	Ru=104,4	Ir=198.	
			Ni=Co=59	Pl=106,6	Os=199.	
H=1			Cu=63,4	Ag=108	Hg=200.	
	Be=9,4	Mg=24	Zn=65,2	Cd=112		
	B=11	Al=27,4	?=68	Ur=116	Au=197?	
	C=12	Si=28	?=70	Sn=118		
	N=14	P=31	As=75	Sb=122	Bi=210?	
	O=16	S=32	Se=79,4	Te=128?		
	F=19	Cl=35,5	Br=80	I=127		
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.	
		Ca=40	Sr=87,6	Ba=137	Pb=207.	
		?=45	Ce=92			
		?Er=56	La=94			
		?Yt=60	Di=95			
		?In=75,6	Th=118?			

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Figure 7. Mendeleev's Periodic Table (Moreno/Lyons productions LLC, 2015)

He arranged the elements into vertical and horizontal rows. There were elements of similar physical and chemical properties in the vertical arrays and they were called groups. In the horizontal rows, there were elements whose properties gradually changed, and the atomic masses increased; these were periods (Mandić et al., 2011). However, unlike the Newlands, Mendeleev did not blindly adhere to series of equal lengths, so that his first period had only two members, the second seven, and the third seventeen (Kepić, 2013). In periods, the gradual change of properties is abruptly interrupted, because the next element has properties that coincide with the properties of the first element in the previous period (Figure 7) (Mandić et al., 2011).

Mendeleev's ideas were presented to the Russian Physical and Chemical Society. Professor Menshutkin introduced them because Mendeleev was ill. His ideas were subsequently published in one of the most widely read chemical journals of the time, the Zeitschrift für Chemie.

Mendeleev was far-sighted enough to predict the existence of undiscovered elements, and he left empty spaces for them. Based on the chemical properties of neighboring elements, he was able to assume their properties. Mendeleev was not the first chemist to do so, but he was the first who recognized the possibility to predict the properties of those elements that were undiscovered. He gave these hypothetical elements names with the prefix *eka*, which means one in Sanskrit, and they were *eka*-boron, *eka*-aluminum and *eka* -silicon, which corresponds to today's elements scandium, gallium and germanium (Figure 8) (Kepić, 2013).

	Predictions	Determinations
	Eka*) - aluminium	Gallium (discovered in 1875 by Lecoq de Boisbaudran)
at. w.	68	69.9
sp. w.	6.0	5.96
at. vol.	11.5	11.7
	Ekaboron	Scandium (discovered in 1879 by Nilson)
at. w.	44	43.79
oxide	Eb_2O_3 sp. w. 3.5	Sc_2O_3 sp. w. 3.864
sulphate	$Eb_2(SO_4)_3$	$Sc_2(SO_4)_3$
bisulphate	not isomorphous with alum	small narrow columns
	Ekasilicon	Germanium (discovered in 1886 by Winkler)
at. w.	72	72.3
sp. w.	5.5	5.469
at. vol.	13	13.2
oxide	EsO_2	GeO_2
sp. w. oxide	4.7	4.703
chloride	$EsCl_4$	$GeCl_4$
boil. pnt. chloride	< 100°	86°
density chloride	1.9	1.887
fluoride	EsF_4	$GeF_4 \cdot 3H_2O$
not gaseous		white solid mass
ethyl compound	$EsAe_4$	$Ge(C_2H_5O)_4$
boil. pnt. ethyl compound	160°	160°
sp. w. ethyl compound	0.96	a little < 1

*) Eka = Prefix being the Sanskrit numeral one

Eka-aluminium	Gallium
Eka-boron	Scandium
Eka-silicon	Germanium
Eka-manganese	Technetium
Tri-manganese	Rhenium
Dvi-tellurium	Polonium
Dvi-caesium	Francium
Eka-tantalum	Protactinium

Figure 8. Mendeleev's postulated elements

(The Chemogenesis Web Book, Mendeleev's predicted elements, 2021)

The first of these elements was gallium, named after a part of France, the homeland of its inventor, Paul-Emile Lecoq de Boisbaudran. Gallium was discovered by de Boisbaudran examining an ore from the Pyrenees and noticing a purple line in the spectrum. He concluded that it originated from a new element and directed his work towards its isolation. The work was extremely difficult because the new element was reluctant to separate from zinc, but at the end he got about 0.1 grams of gallium. Examining its properties, he saw the resemblance to Mendeleev *eka* –aluminum. This was just the beginning of the confirmation of the Periodic Table of the Elements (Kepić, 2013).

In 1879, another postulated element, the *eka*- boron, was discovered. It is called scandium. When the Swedish chemist Nilson (Lars Fredrik Nilson) realized that he was dealing with a new element, he saw that its properties coincided with *eka*-boron, which accelerated its confirmation (Kepić, 2013).

The third postulated element was *eka*-silicon, germanium. German chemist Clemens Alexander Winkler sent a silver mineral for analysis. He soon realized that there was a certain amount of an unknown element in the mineral, so he tried to identify it by spectroscopic methods. However, it failed, because germanium has wavelengths in the ultraviolet part of the spectrum. He then turned to classical methods, first converting the element to oxide, and then reducing it. At first, they wanted the element to be called neptunium, because its existence was predicted before the discovery, as in the case of the planet Neptune. In the end, he called it germanium, part of his country (Kepić, 2013).

The later discovered elements, such as technetium, rhenium, polonium, astatine, francium, and radium, fitted very easily into the table formed in this way. This was especially facilitated by the fact that their properties could be assumed, which means that the researchers could focus their efforts on the targeted discovery of an element (Kepić, 2013).

Another important thing that Mendeleev did was to correct incorrectly determined atomic masses. At that time, the relative atomic mass (then called atomic weight) was measured using the following formula:

atomic weight = equivalent weight x valence

Equivalent weights were usually correct, but sometimes the element would be assigned the wrong valence. To preserve the rule that chemically similar elements come one below the other, he had to correct the atomic mass of beryllium from 13.5 to 9, because it was given a valence of 3, due to its chemical similarity to aluminum. With the correction, beryllium came above magnesium, to the place that really belongs to. In two more cases he corrected the atomic masses and put tellurium in front of iodine and cobalt in front of nickel. Although he was wrong this time as far as atomic masses are concerned, these four elements took their places in the Periodic Table of the Elements. This anomaly was explained when the existence of different isotopes of one element was detected (Kepić, 2013).

Sima Lozanić, famous Serbian chemist, was among the first in the world to accept Mendeleev's system (Wikipedija, Sima Lozanić, 2021).

Of course, Mendeleev continued to correct the shortcomings of the Periodic Table, to publish his Periodic Table in a new form, with groups of similar elements arranged in columns rather than rows. These columns were marked with Roman numerals (from I to VIII), which corresponded to the oxidation state of each element. He also made detailed predictions regarding the properties of the elements, which he previously pointed out as undiscovered, but which should exist. He presented his achievements to the foreign scientific public and published his work in the German journal Liebigs Annalen in 1871 (Wikipedija, Dmitrij Mendeljejev, 2021).

The significance of atomic numbers for the organization of the Periodic Table was not considered important until the existence and properties of protons and neutrons were understood. Atomic weight was used in predicting the properties of undiscovered elements more accurately than any other method known at the time (Wikipedia, Dmitrij Mendeljejev, 2021).

Later, in 1913, the English physicist Henry Moseley determined the experimental values of the nuclear charge *i.e.*, the atomic number of individual elements. These results confirmed that Mendeleev's distribution of elements is according to atomic numbers (Wikipedia, Henry Moseley, 2021).

As the discovery of the structure of the atom followed many years after the Periodic Table, Mendeleev's effect is even more impressive (Editorial, 2019).

One thing that Mendeleev did not foresee was the discovery of a whole group of elements, noble gases, which were found in the last decade of the 19th century by the Scot William Ramsay together with his colleagues. Mendeleev was disappointed at first. He initially rejected Ramsay's discovery of argon, which nevertheless further improved periodic laws, so chemists finally realized that argon was part of a completely new group of chemical elements (Opusteno.rs, 2018). The existence of elements with zero valence between two groups of valences exactly coincided with Mendeleev's previously rejected idea that the valences of groups of elements are alternately even and odd numbers (Kostić, 2010). Before he died in 1907, Mendeleev realized that Ramsay's findings did not contradict the system, but further proved it. Ramsay received the Nobel Prize for discovering five elements. Mendeleev never received that honor. Maybe because his discovery took root so quickly in the world of science, which, due to its simplicity, seems to have always been there. Nevertheless, one element with atomic number 101 is named after him - Mendelevium. The creator of the Periodic Table of the Elements certainly deserved something like that (Opusteno.rs, 2018).

If we say that Lavoisier initiated the first revolution in chemistry by putting it on the right track, Mendeleev is certainly responsible for the second revolution which confirmed the correctness of movement on that track (Kepić, 2013).

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Conflict-of-Interest Statement

None.

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