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A Modern View of Anomalies in the Metal Groups of the Periodic System of D.I.Mendeleev

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The article is devoted to the 150th anniversary of the Periodic Table of Chemical Elements by D.I.Mendeleev. The fundamental law of nature, discovered by D.I.Mendeleev has anomalies and paradoxes associated with certain groups of metals. When studying the physical and chemical properties of complex metal compounds, many discrepancies can be found, namely, the location of elements in groups, which primarily relate to metals with different valences. By studying the approaches and methods for predicting the arrangement of chemical elements, it can be established that D.I.Mendeleev eliminated many differences for some metals during the formation of the Periodic system of chemical elements. D.I.Mendeleev developed a principle that excludes such errors when finding and discovering new elements. Analytical studies conducted by a Russian scientist helped to calculate the atomic masses and describe the properties of three elements not known at that time – «eka-boron», «eka-silicon», «eka-aluminum», the existence of which was proved and confirmed by subsequent discoveries of scandium, germanium, boron, and gallium. The paper provides a significant assessment of the forecasting of metals in various groups of the periodic system. Changes in the properties of some metals significantly influenced their location in the table of D.I.Mendeleev.

Key words: table of D.I.Mendeleev; metals; groups; periods; chemical properties; eka elements; Saint-Petersburg Mining University

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Introduction. The building of chemical foundations in the 19th century forgotten during the period of intellectual breakthrough (the discovery of the laws of quantum mechanics, nuclear physics, the creation of the theory of relativity) became a revolution that made it possible to explain the modern world [11]. On December 20, 2017, the UN General Assembly declared 2019 the International Year of the Periodic Table of Chemical Elements by D.I.Mendeleev in connection with the 150th anniversary of the discovery of the law of chemical elements by D.I.Mendeleev. Previously, this initiative was put forward by the Russian Federation within the framework of UNESCO and was approved at the 39th session of the General Conference.

Of all known and discovered chemical elements, about 90 are metals. Most inorganic compounds are metallic compounds represented in oxide form. In nature, metals can be found in free form, for example, native mercury, silver, and gold, but most often, they are in the form of complex compounds [5].

There are several types and variants of the classification of metals, depending on the structure and form of the periodic tables [18]. The most orderly is the classification of metals by their location in the periodic system of elements, i.e. chemical classification.

Features of the discovery of the Periodic Law of D.I.Mendeleev. As a result of great efforts and long, painstaking work, D.I.Mendeleev discovered the Periodic Law on February 17 (March 1), 1869. This discovery was associated with great difficulties, since the atomic masses of many elements, especially the metals of beryllium, cerium, vanadium, titanium, were 1.5-2 times less or more than the true ones, and erbium and didymium were mixtures of several elements. These difficulties existed until the errors in the definitions of atomic masses were eliminated. Mendeleev published the first version of the table in one of the first editions of his textbook, Fundamentals of Chemistry (1871). The first table still had many empty cells left for undiscovered elements (Fig.1).

D.I.Mendeleev, having read Paul Emil Lecock de Bois Baudodran's report on the discovery of gallium, immediately recognized his predicted «eka-aluminium» from some of its properties and

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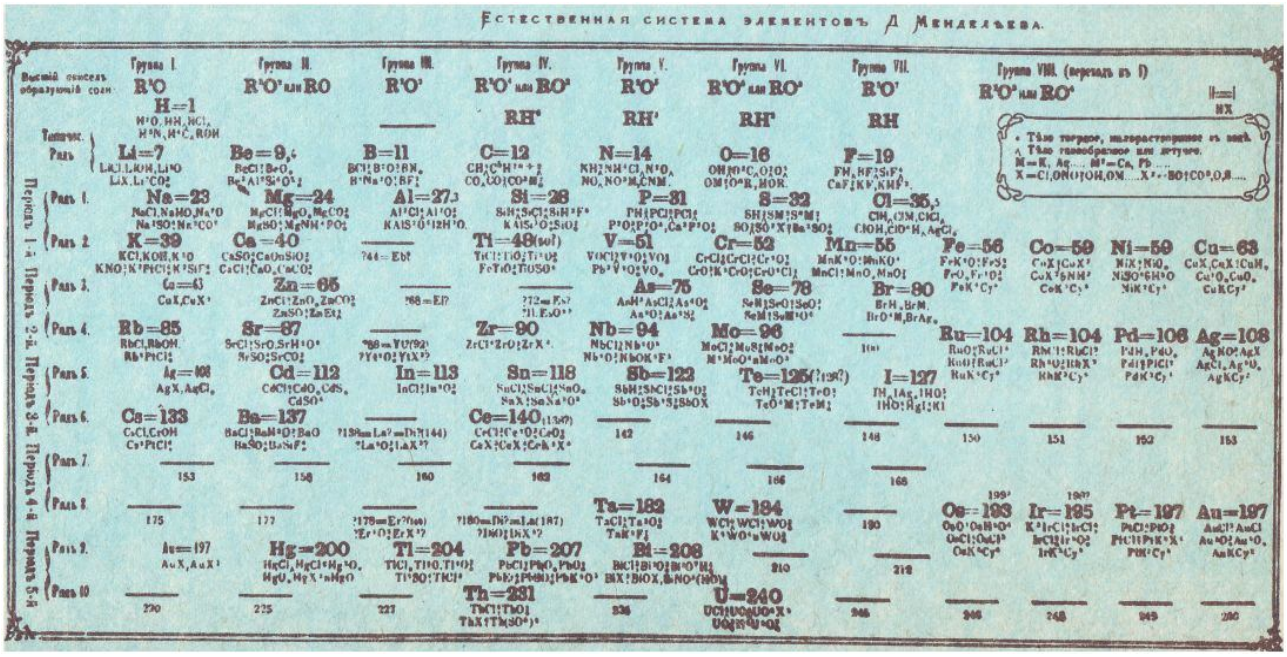


Fig. 1. The natural system of elements of D.I.Mendeleev (1871)

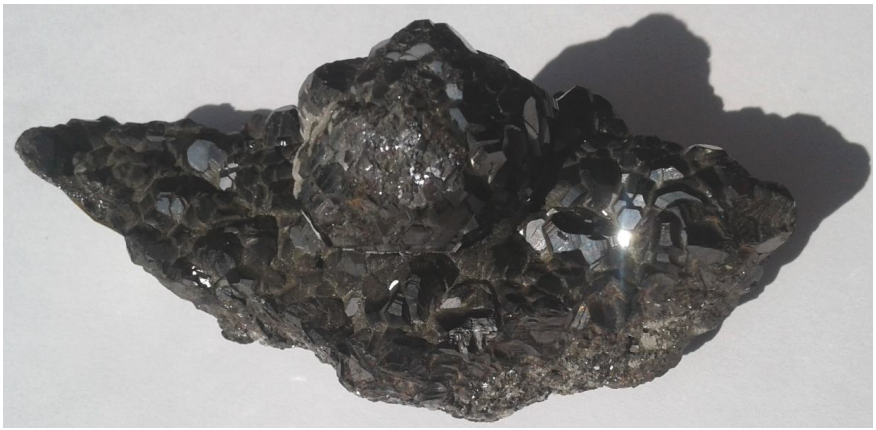


Fig.2. Sphalerite sample

pointed out to the French chemist the error in determining the density of gallium, which, as a result, the author of the discovery finally acknowledged [14]. Figure 2 shows sphalerite, from which gallium was first obtained.

Colleagues from the Freiberg Academy presented archival information about a similar paradoxical situation, which repeated when indium was accidentally discovered. German chemists Ferdinand Reich and Theodor Richter isolated sulfide of an unknown metal from zinc blende; upon spectroscopic examination, they found a bright blue glow in the spectrum (indigo color), due to which this element was called «indium», but its valency was further mixed up, which led to the wrong location in another subgroup of metals (Fig.3).

The final confirmation of the outstanding discovery and approaches made by the great Russian scientist, according to many respected chemists, occurred when the eka-silicon predicted by D.I.Mendeleev [13] was discovered by Clemens Winkler in 1886 in Saxony. The element was named «germanium» like gallium and scandium in honor of the country where it was discovered. Doubts arose when C. Winkler decided that he had discovered an analog of antimony, and this, therefore, was an element from the fifth group. But D.I.Mendeleev wrote to the German scientist about his mistake, a place for germanium was already predicted 15 years ago in the 4th group, in the 5th row, in cell number 29, i.e., its location should be between titanium and zirconium. Later, a

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Fig. 3. Sample of indium donated to the Mining Institute of Empress Catherine II by the Freiberg Mining Academy in 1867

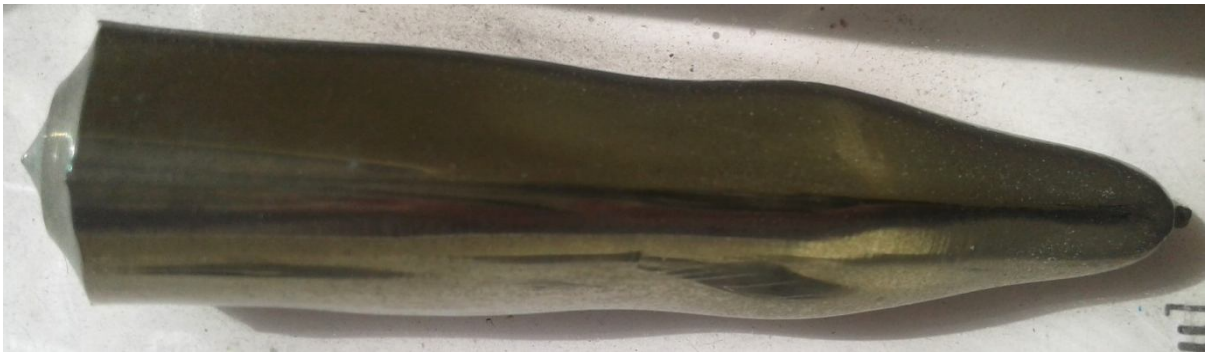


Fig. 4. Single crystal of germanium (1964, Leningrad Mining Institute)

German scientist admitted his mistake. Figure 4 shows a single crystal of germanium; the sample was obtained at the G.V.Plekhanov Leningrad Mining Institute (now Saint-Petersburg Mining University) in 1964.

The meeting of D.I.Mendeleev and C.Winkler in Berlin [16] is well known, and they resolved many issues, primarily related to the arrangement of metals in groups and periods by their atomic mass and valency. The materials obtained from the library of the Freiberg Mining Academy and studied by the authors together with German scientists after 135 years of discovery of these elements fully confirm the chain of events of that time. Thus, after germanium took its place, metals and other chemical elements were located in the table in eight groups in each row and from top to bottom there were 4-6 elements in each column, and the elements in one column were close to each other in their chemical properties, and their physical properties naturally changed depending on the increase in the atomic mass of the element [17]. D.I.Mendeleev saw the mistake of the previous classifications of elements in the fact that these elements were put in places on the basis of one attribute (atomicity) taken in isolation from other properties, he said, «based on one isolated property it's impossible to build a stable classification»; therefore, the unordered classification of chemical elements inevitably led to instability of the study of the forms of compounds.

When considering the similarity of the elements in the table diagonally, it is obvious [15] that the chemical properties of beryllium are largely similar to the properties of aluminum. Aluminum, like beryllium, dissolves in alkali solutions but is not exposed to concentrated hydrochloric acid. Therefore, there was a paradox when for a long time everyone considered it trivalent and attributed to it the wrong atomic mass. This mistake was corrected precisely by D.I.Mendeleev, after discovery of the Periodic Law [7].

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Aluminum is one of the most common elements in the earth's crust, located in the periodic table of D.I.Mendeleev at number 13 and has unique physical-chemical properties. Aluminum is credited with several paradoxical and mystical properties [1]. Like beryllium, aluminum, which was discovered long before the Periodic Law [19], is found in various minerals, which are especially common in aluminosilicates (Fig.5).

Given the specifics of D.I. Mendeleev's works and research on the relationship of mineral raw materials with the arrangement of elements, it can be assumed that the ideology and structure of the table itself were formed around this metal. It is confirmed by the properties of the «predicted» elements with the traditional prefix «eka» – «eka-aluminium» and the metals «aluminum-gallium-indium-titanium» placed later in the period. At present, the best modifying additive for aluminum alloys is Al-Ti-B alloys [9, 22]. In this case, we can talk about building and improving properties due to the combined influence of metals of this period.

Many paradoxes exist in metal groups of elements such as mercury, copper, silver, platinum, and especially gold, which are found in nature in a native form. On the one hand, we do not know who discovered each of these elements; it has been known for their existence for more than two millennia, on the other hand, all the works of alchemists have been devoted to these metals. Figures 6-7 show samples of native gold and platinum donated to the Mining Institute of Empress Catherine II by the St. Petersburg Mint in 1887.

The main goal of the experiments was to obtain gold from various combinations of metals and their compounds. The essence of these assumptions and hypotheses was reduced to transition states of some elements up to the replacement of some properties [24]. It is known [20] that D.I.Mendeleev attributed all the alchemical works to the anti-scientific topics, and theories of transforming one element into another, «all attempts of this kind have so far been in vain and have turned out to be only hollow speculations or experimental errors, and therefore established and generally accepted there is no reason to go to the fantastic and arbitrary, firmly established and generally accepted here it must be considered, alas, so far only negative, namely, that no one has ever encoun-



Fig.5. Sample of aluminum casting. A gift from the Krasnoyarsk Aluminum Plant to the Leningrad Mining Institute, 1974



Fig.6 Sample of native gold «Tube», weight 744.73 g, Yekaterinburg area, Ural, Russia. Donated by the St. Petersburg Mint, 1887



Fig.7. Platinum sample, weight 5112.25 g, Nizhny Tagil, Ural, Russia. Donated by the St. Petersburg Mint, 1887

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tered a single phenomenon in which one simple body would turn into another, so we can make the hypothetical conclusion, which is the basis of all our science that chemical elements are independent, they need to limit the knowledge about the transformation of substances into each other» [25].

A modern view at the table of D.I.Mendeleev. Currently, due to the development of technical means and conditions, a high level of analytical instruments, the opportunity has appeared to «study from a new perspective» the structural changes and their correspondences associated with mechanical properties. We are talking about alloys, ligatures, modifiers, additives and the synthesis of multicomponent materials with unique properties [23]

Of the 17 elements related to rare-earth elements (REE), D.I.Mendeleev considered only five – lanthanum, cerium, didymium, erbium, and yttrium [6]. It was the introduction of didymium into the first version of the periodic system that later helped to decipher it as a mixture of neodymium and praseodymium. These two elements are the main addition elements in alloys. Erbium and yttrium, elements that had already been discovered by then, also were a mixture of several elements and contained a rather large amount of gadolinium, dysprosium, holmium, thulium, ytterbium, lutetium, and scandium. The problems of separation of the rare-earth elements of the heavy and light groups were well known to D.I.Mendeleev and the scientists of that time, especially the experimental difficulties associated with their isolation.

The formation of a group of rare-earth elements in the table contributed to the development of nanotechnology when even a minor input of one or another element led to a fundamental change in structure and properties and created the prerequisites for creating new composite and multifunctional materials. For example, it became possible to create aluminum alloys modified with scandium and yttrium, the properties of which correlate with steel products [21].

There is a stable paradigm in the technical literature [8] that if in the full version of the periodic table a straight line is drawn through the elements boron and astatine, then metals will be located to the left of this line, and the right of it the whole group of non-metals (Fig.8). The first questions (paradoxes) concerning the table and the location of already discovered metals were raised by D.I.Mendeleev, regarding the separation of metals into two fundamental groups – intransitive and transitional. So, Mendeleev placed beryllium immediately after lithium, attributing to it an atomic mass of 9.4 instead of 13.5, as other chemists thought. He placed thorium in one group (IV) with titanium, although this should not have been done at all, given the data on their atomic masses [16].

An analysis of the documents showed [12] that, during the creation of the table, the values of the atomic masses of the elements were periodically updated, but there were still errors in the de-

Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIIIa		Iб	IIб	IIIб	IVб	Vб	VIб	VIIб	VIIIб
															H	He
Li	Be	M-elements									B	C	N	O	F	Ne
Na	Mg										Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**Ac														
		T- elements									B1- elements			B2- elements		
*Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	R- elements		
**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	-	TR- elements		

Fig.8. Division of the table of D.I.Mendeleev into metals and non-metals [14]

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termination of valency; therefore, the arrangement of the elements in one sequence or another led to errors of a significant nature.

Errors in the values of atomic masses were sometimes very large, but D.I.Mendeleev managed to determine the corresponding sequence of elements that coincided with their ordinal (atomic) numbers. On the other hand, metals, unlike many elements, have more stable forms, especially in oxide compounds, which made it possible to determine their locations in the table with virtually no errors.

In addition to the chemical arrangement of metals in the table, there is also, although not a generally accepted, but long-established technical classification of metals, divided into two distinct groups – non-ferrous and ferrous metals. Moreover, in non-ferrous metals, three pronounced subgroups are light, heavy, and noble metals [10]. A group of rare metals, separate from rare-earth metals (REM), is usually considered to be involved. This arrangement of metals is paradoxical and not as logical as chemical because it is based on the constantly changing properties of metals, which depend on their valency. The explanation of how regular «mass jumps» affect the chemical properties of elements cannot be ordinary. The existing theory of the structure of atoms proceeds from the fact that the magnitude of the charge of the nucleus completely determines the structure of the electron shells, and the structure of the nucleus, whatever it is, does not affect the behavior of valence electrons.

Thus, there are three worthy generalizations of D.I.Mendeleev that is not appreciated: the changing properties of elements concerning transition metals, the functions of atomic mass, and its correspondence with number theory, an instrument for understanding periodicity. All these factors are combined in a table into a single whole, but on the other hand, when viewed with a modern eye and going beyond the framework of classical quantum mechanics as a paradox, there are cardinal changes in the properties and structures of some elements when they correspond to groups and periods [3].

In another embodiment, when there are no clear boundaries [2], iron and alloys (steel and cast iron) based on it are classified as ferrous metals. In this interpretation, light (Li, Be, Mg, Ti, Al) and heavy metals (Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Sn, Pb, etc.) are distinguished, as well as refractory groups (Zr, Hf, V, Nb, Ta, Cr, Mo, W, Re), precious (Ag, Au, platinum metals) and radioactive (U, Th, Np, Pu, etc.) metals, and only then they are released according to the laws of geochemistry scattered (Ga, Ge, Hf, Re) and rare (Zr, Hf, Nb, Ta, Mo, W, Re) metals. There are 22 transition metals (Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi, Po), which are located in the main subgroups of the periodic system and are characterized by the fact that in their atoms there is a sequential filling of the electronic levels s and p.

Transition metals are located in subgroups and are characterized by the filling of *d*- or *f*-electronic levels. The *d*-elements include 37 metals of subgroups: Cu, Ag, Au, Zn, Cd, Hg, Sc, Y, La, Ac, Ti, Zr, Hf, Rf, V, Nb, Ta, Db, Cr, Mo, W, Sg, Mn, Tc, Re, Bh, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Hs, Mt. The *f*-elements include 14 actinides (Th, Ra, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr). Among the transition metals, rare earth metals (REM), such as Sc, Y, as well as a group of lanthanides (Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Du, But, Er, Tm, Ub, Lu) are also distinguished. Platinum metals (Ru, Rh, Pd, Os, Ir, Pt) are also transition metals, as are transuranium metals (Np and other elements with a larger atomic mass).

The paradoxes of such an arrangement of elements in the table include the fact that D.I. Mendeleev placed elements with a large atomic mass in front of elements with a lower atomic mass, for example, potassium, tellurium, nickel, and cobalt. It turned out that the tellurium core charge is 52, and the iodine charge is 53, the argon core charge is 10, and potassium is 11, etc. [4].

In other words, there is some anomaly associated with certain properties that do not change the basic position regarding certainty. In the aggregate of all the properties taken as a whole, each element occupies a distinct place in the periodic system. The abnormalities in the increase in atomic masses are similar to permutations that cannot make one doubt the correctness of the law, although

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Fig.9. Interactive Periodic Table of Mendeleev

D.I.Mendeleev personally was inclined to think that in this case, the discrepancies are explained by experimental errors in determining atomic mass.

Saint-Petersburg Mining University honors the memory of the russian scientist D.I.Mendeleev. The scientific library contains 25-lifetime editions of scientific articles by D.I.Mendeleev. In the halls of the Mining Museum there are many exhibits dedicated to the great scientist, the Periodic Table of Mendeleev, which allows you to consider each element, is especially interesting for conducting studies. An interactive table of chemical elements, which has no analogs in Russia, was donated to the Mining University by the PhosAgro company (Fig.9).

D.I.Mendeleev was a teacher of D.P.Konovalov, director of the Mining Institute (1903-1905). It was D.P.Konovalov who initiated the construction of a new chemical laboratory of a European level at the Mining Institute following the ideas of D.I.Mendeleev.

Conclusion. The periodic law is universal and refers to such general scientific laws that exist in nature, and therefore, in the process of the evolution of our knowledge, they will never lose their significance. After the works of D.I.Mendeleev it was established that not only the electronic structure of the atom but also the fine structure of atomic nuclei obeys the periodicities, which indicates the periodic nature of the properties in the world of elementary particles.

The Russian Academy of Sciences and the Russian Chemical Society in the year of the 150th anniversary of the Periodic Law, declared by the United Nations as the International Year of the Periodic Table of Elements, are actively looking for ways to restore the Mendeleev word about periodicity to use it as a means of breaking through new, unexplored depths of the creation and structure of matter.

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