**LECTURE TEXT**

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# The short form of Mendeleev's Periodic Table of Chemical Elements: toolbox for learning the basics of inorganic chemistry. A contribution to celebrate 150 years of the Periodic Table in 2019

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## Abstract

A condensed overview about the forefathers' and Mendeleev's contribution to the compilation of the Periodic Table of Chemical Elements is presented. Milestones en route to the modern Periodic Table are 'electrification' of the Periodic Law, discovery of the rare-earth elements and the noble gases, investigation of the atomic structure and discovery of the transuranic elements. Then the contribution focuses on the Table's short form as toolbox for learning the basics of inorganic chemistry. Similarities and differences in the chemical behavior of elements on the basis of full, close and approximate electronic analogies and the kainosymmetric sublevels ($1s$, $2p$, $3d$, $4f$) are described. A question/answer section completes the article.

**Keywords** Periodic Table · Mendeleev · Lothar Meyer · Electronic analogies · Kainosymmetric sublevels

## Introduction

One of the most difficult challenges a freshman student of inorganic chemistry comes across is to remember a vast amount of information about the properties of chemical elements and their compounds. It is inefficient and also boring for an intellectually curious student to memorize each particular reaction and characteristic. In fact, the information should be presented in a systematic way with the maximum use of regularities, similarities and analogies.

Such guidance is provided by the Periodic Law, which is presented as Periodic Table of Chemical Elements, a tabular arrangement of the chemical elements, ordered by their atomic numbers and electron configurations. The development of the Periodic Table of the Elements is one of the most significant achievements in science and a uniting scientific concept with broad implications in chemistry, physics, biology, astronomy and other natural sciences. It is used by chemists to arrange and classify new information and helps the students especially during their first year to feel confident.

The first part of the article covers the milestones en route to the modern Periodic Table, while its second part is focused on the Table's short form as toolbox for learning the basics of inorganic chemistry. A question/answer section completes the article.

### The forefathers of the Periodic Table

It is fascinating to follow the different approaches of our chemist-forefathers to establish a reasonable system of the chemical elements [1–4]. We should not forget that about 250 years ago, when the first ideas were formulated, only a fraction of the elements we know today was known then.

### Early classifications of the chemical elements

Although the Russian chemist Dmitri Ivanovich Mendeleev (February 8, 1834–February 2, 1907) is recognized worldwide as the 'father' of the Periodic Table, the work of many scientists contributed to its present form.

There are two necessary prerequisites to the construction of the Periodic Table.

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## The discovery of individual elements

The ancient Greeks regarded fire, air, water and earth as the 'elements' constituting the world. The 12 elements copper, lead, gold, silver, iron, carbon, tin, sulfur, mercury, zinc, arsenic and antimony have been known and used since ancient times. Based on the ideas of the Anglo-Irish polymath Robert William Boyle (1627–1691) and the French nobleman and chemist Antoine-Laurent de Lavoisier (1743–1794), the modern definition of the 'element' has been coined. At that time light and heat were still regarded as 'elements'.

Boyle defined an element as a material that can be identified by scientific experiment and can not be broken down chemically into simpler substances. This is the definition that is still in use today.

Lavoisier was the first, who interpreted a chemical element as an isolable material substance, rather than as an abstract property or principle. His diagrammatic summary categorizes 'elements' (light, heat, O, N, H) and 'simple substances' (metals, nonmetals and salifiable earths). Elaborations of Lavoisier's classification, based largely on a consideration of the elements' acid–base properties and the reducibility of the corresponding oxides, were made in the early decades of the nineteenth century by Swedish chemist Jöns Jacob Berzelius (1779–1848), French chemist Louis-Jacques Thénard (1777–1857) and Scottish chemist and mineralogist Thomas Thomson (1773–1852).

The first scientific discovery of an element occurred in 1669, when the German merchant and alchemist Hennig Brand (born 1630, year of death unknown) discovered the nonmetal phosphorus. During the next 200 years, a vast body of knowledge concerning the properties of elements and their compounds was acquired by chemists. By 1869, a total of 63 elements had been discovered. As the number of known elements grew, scientists recognized patterns in their properties and began to develop classification schemes.

## The determination of atomic masses

Lavoisier revolutionized chemistry in the eighteenth century by introducing accurate weighing of substances, including gaseous matter. He observed that a given amount of matter has a mass that remains the same when it is redistributed from one chemical combination to another, whether in the solid, liquid, or gaseous state. The analysis of the French chemist Joseph Louis Proust (1754–1826) showed that a particular chemical compound always contained the same elements united in the same proportions by mass ('weight'). The English chemist John Dalton (1766–1844) and Berzelius were the first to determine atomic masses. The relative atomic mass was originally defined relative to that of the lightest element, hydrogen, which was taken as 1.00. The

Italian chemist Stanislao Cannizzaro (1826–1910) refined in the 1860s the atomic mass[1] by applying Avogadro's Law: the different quantities of the same element contained in different molecules are all whole multiples of the atomic mass.

In 1864 the British chemists William Odling (1829–1921) and Alexander William Williamson (1824–1904) suggested independently classifications of the chemical elements based on the valence values of their atoms rather than on the basis of metallicity of the 'simple substances' and the acid-base properties of their oxides.

The comprehensive IUPAC (International Union of Pure and Applied Chemistry) Technical Reports from 2000 [5] and 2013 [6] provide useful information about the history and methods of determining atomic masses.

## Law of Triads

In 1817, the German chemist Johann Wolfgang Döbereiner (1780–1849) noticed that the atomic mass of strontium fell midway between the atomic masses of calcium and barium, elements possessing similar chemical properties. In 1829, after discovering the halogen triad composed of chlorine, bromine and iodine and the alkali metal triad of lithium, sodium and potassium, he proposed that nature contained triads of elements, the middle element had properties that were an average of the other two members when ordered by their atomic masses (the Law of Triads).
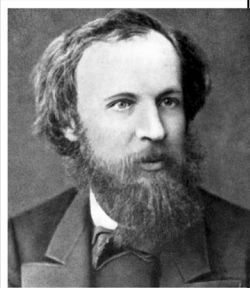
This new idea of triads became a popular area of study. Between 1829 and 1858 the Frenchman Jean Baptiste André Dumas (1800–1884), the American Josiah Parsons Cooke (1827–1894) and the Germans Leopold Gmelin (1788–1853), Ernst Lenssen (born 1837, year of death unknown) and Max Joseph von Pettenkofer (1818–1901) found that these types of chemical relationships extended beyond the triads. In 1886, fluorine was discovered and added to the halogen group. Oxygen, sulfur, selenium and tellurium were grouped into a family while nitrogen, phosphorus, arsenic, antimony, and bismuth were classified as another.

## First attempts designing a Periodic Table

If a Periodic Table is regarded as an ordering of the chemical elements demonstrating the periodicity of chemical and physical properties, credit for the first Periodic Table

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[1] The modern definition of the atomic mass (often incorrectly called 'atomic weight') is the average mass of all naturally occurring isotopes of an element. Since 1961 the atomic mass unit (amu) is defined using carbon's most common isotope $^{12}C$ as the reference standard. The molar mass (g $mol^{-1}$) is defined as the amount of a given substance (chemical element or chemical compound) per mole ($6.022 \times 10^{23}$) atoms or molecules.

**Fig. 1** Dmitri Ivanovich Mendeleev's (Дмитрий Иванович Менделеев) Periodic Table (1869)



Mendeleev as young professor at St. Petersburg University

ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВЕСЬ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

Mendeleev as renowned scientist

(published in 1862) should be given to the French geologist Alexandre-Émile Béguyer de Chancourtois (1820–1886). De Chancourtois transcribed a list of the elements positioned on a cylinder in terms of increasing atomic mass. When the cylinder was constructed with 16 mass units written on the cylinder per turn, closely related elements were lined up vertically. This led de Chancourtois to propose that 'the properties of the elements are the properties of numbers'. De Chancourtois was first to recognize that elemental properties reoccur every seven elements. Using this chart, he was able to predict the stoichiometry of several metallic oxides. As a drawback, his chart included some ions and compounds in addition to elements.

In 1864, the British chemist John Alexander Reina Newlands (1837–1898) had discovered periodicity in the form of his Law of Octaves, so called because the properties of the elements repeated every eighth element, like the notes of the musical scale.

## Mendeleev: father of the Periodic Table
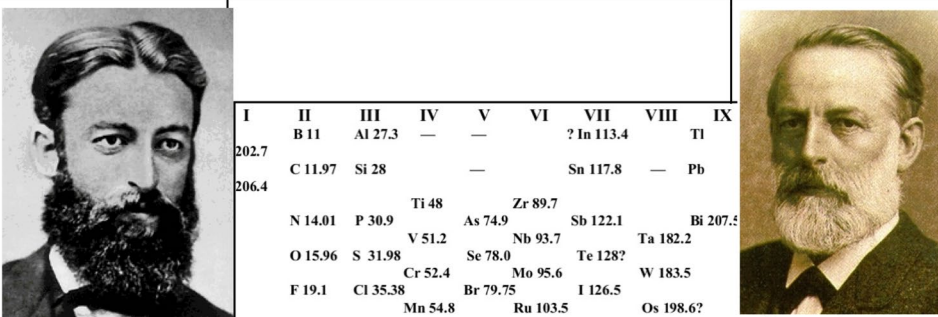
The Russian Dmitri Ivanovich Mendeleev (1834–1907) and the German Julius Lothar Meyer (1830–1895) were contenders in the race to develop a Periodic Table of the chemical elements. Both chemists produced remarkably similar results at the same time working independently from one another. For both Mendeleev and Meyer, writing a textbook proved to be the impetus for developing the Periodic Table. Meyer's textbook from 1864 [7] included an abbreviated

version of a Periodic Table with 28 elements. Hence, it contained about half of the known elements listed in order of the atomic masses and demonstrated periodic valence changes as their function. In 1868, Meyer constructed an extended Table with 52 elements which he gave to the chemist and physicist Adolf Ferdinand Weinhold (1841–1917), who was also his brother-in-law, for evaluation. Mendeleev's Periodic Table became available to the scientific community in 1869 (Fig. 1) through publication in the main German chemistry periodical of the time [8, 9], before Meyer's (Fig. 2) appeared in 1870 [10].

In constructing his Periodic Table, Mendeleev assumed that apparent exceptions to his law were the result of three possible causes: (1) incorrect valence values, (2) incorrect atomic masses, (3) the presence of, as yet, undiscovered elements.

From the gaps present in his Periodic Table, Mendeleev predicted the existence of the four elements eka-aluminum (atomic number 31), eka-boron (21), eka-silicon (32) and eka-manganese (43) (eka: as-yet undiscovered element). In the case of the three so-called patriotic elements gallium [discovered in 1875 by the Frenchman Paul-Émile Lecoq de Boisbaudran (1838–1912)], scandium [discovered in 1879 by the Swede Lars Fredrik Nilson (1840–1899)] and germanium [discovered in 1886 by the German Clemens Alexander Winkler (1838–1904)], the predictions of their properties by Mendeleev were amazingly correct. In Table 1 the predicted properties of eka-silicon are compared with the determined ones of germanium.

Fig. 2 Julius Lothar Meyer's Periodic Table with vertical display of periods (1870)



The young Meyer around 1867

Julius Lothar Meyer as renowned scientist

| I | II | III | IV | V | VI | VII | VIII | IX |
|---|----|-----|-----|----|-----|-----|------|-----|
| 202.7 | B 11 | Al 27.3 | — | — |  | ? In 113.4 |  | Tl |
| 206.4 | C 11.97 | Si 28 |  | — |  | Sn 117.8 | — | Pb |
|  |  |  | Ti 48 | Zr 89.7 |  |  |  |  |
|  | N 14.01 | P 30.9 |  | As 74.9 | Nb 93.7 | Sb 122.1 | Ta 182.2 | Bi 207.5 |
|  |  |  | V 51.2 |  |  |  |  |  |
|  | O 15.96 | S 31.98 |  | Se 78.0 | Mo 95.6 | Te 128? | W 183.5 |  |
|  |  |  | Cr 52.4 |  |  |  |  |  |
|  | F 19.1 | Cl 35.38 |  | Br 79.75 |  | I 126.5 |  |  |
|  |  |  | Mn 54.8 | Ru 103.5 |  | Os 198.6? |  |  |
|  |  |  | Fe 55.9 | Rh 104.1 |  | Ir 196.7 |  |  |
|  |  |  | Co&Ni 58.6 | Pd 106.2 |  | Pt 196.7 |  |  |
| Li 7.01 | Na 22.99 | K 39.04 |  | Rb 85.2 | Cs 132.7 | Au 196.2 |  |  |
|  |  |  | Cu 63.3 | Ag 107.66 | Ba 136.8 |  |  |  |
| ?Be 9.7 | Mg 23.9 | Ca39.9 |  | Sr 87.0 |  |  |  |  |
|  |  |  | Zn 64.9 | Cd 111.6 |  | Hg 199.8 |  |  |

Table 1 Properties of eka-silicon (predicted by Mendeleev) and germanium (experimentally determined)

| Property | Eka-silicon | Germanium |
|----------|-------------|-----------|
| Molar mass (g mol$^{-1}$) | 72 | 72.59 |
| Molar volume (mL mol$^{-1}$) | 13 | 13.6 |
| Density (g mL$^{-1}$) | 5.5 | 5.35 |
| Melting point (°C) | High | 947 |
| Color | Gray | Gray |
| Occurrence | Titanium and zirconium minerals | Not verified |
| Oxide | $EsO_2$ | $GeO_2$ |
| Density of $EsO_2$ (g mL$^{-1}$) | 4.7 | 4.70 |
| Chloride | $EsCl_4$ | $GeCl_4$ |
| Density of $EsCl_4$ (g mL$^{-1}$) | 1.9 | 1.88 |
| Boiling point of $EsCl_4$ (°C) | 57–100 | 83 |
| Ethyl compound | $Es(C_2H_5)_4$ | $Ge(C_2H_5)_4$ |
| Density of $Es(C_2H_5)_4$(g mL$^{-1}$) | 0.96 | 0.99 |
| Boiling point of $Es(C_2H_5)_4$ (°C) | 160 | 163 |

The fascinating story of the discovery of germanium by Winkler in the mineral argyrodite ($Ag_8GeS_6$) is presented in [11].

Technetium (eka-manganese) was isolated by Italian mineralogist Carlo Perrier (1886–1948) and Italian-American physicist Emilio Segrè (1905–1989) in 1937, well after Mendeleev's lifetime, from samples of molybdenum that had been bombarded with deuterium nuclei in a cyclotron. Mendeleev had predicted an atomic mass of 100 amu in 1871; the most stable isotope of technetium $^{98}$Tc has an atomic mass of 97.907215 amu.

In addition to the fact that Mendeleev's Table was published before Meyers', it was the accuracy of the predicted missing elements that played the key role in the acceptance of Mendeleev's work by the chemical community in the late 1870s and early 1880s. The advantage of Mendeleev's Periodic Table over previous attempts was that it exhibited similarities not only in small units such as the triads, but showed similarities in an entire network of vertical, horizontal, and diagonal relationships.

In 1905, Mendeleev was elected a member of the Royal Swedish Academy of Sciences. The following year the Nobel Committee for Chemistry recommended to the Swedish Academy to award the 1906 Nobel Prize in chemistry to Mendeleev for his discovery of the Periodic Law. The Chemistry Section of the Swedish Academy supported this recommendation. The Academy was then supposed to approve the Committee´s choice, as it has done in almost every case. Unexpectedly, at the full meeting of the Academy, a dissenting member of the Nobel Committee, the Swedish chemist Johan Peter Clason (1848–1937), proposed the candidacy of the French chemist Ferdinand Frederick Henri Moissan (1852–1907) for his work in isolating fluorine from its compounds. The Swedish physicist and physical chemist Svante August Arrhenius (1859–1927) had great influence in the Academy. Arrhenius was not a member of the Nobel Committee for Chemistry, however, a member of the Committee for Physics. According to the regulations, both Committees were involved in the chemistry and physics Nobel Prizes. Arrhenius pressed for the rejection of Mendeleev, arguing that the 37-year-'old' Periodic Table was too old for acknowledging its discovery in 1906. According to the contemporaries, Arrhenius was motivated by the grudge he held against Mendeleev. Mendeleev could not accept Arrhenius' 'physical' solution theory, including the existence of ions. Instead, he developed a 'chemical' solution theory where the formation of a solution was considered as a chemical reaction. After heated arguments, the majority of the Academy voted for Moissan.

The book Nobel Prize—The Road to Stockholm [12] describes the process of selection of the laureates, discusses the ingredients for scientific discovery and for getting recognition. It reviews the decisive moments of scientific careers en route to the Nobel Prize. It reveals the human face of scientists and the human side of their endeavors.

In 1955, a synthetic element was discovered by bombarding einsteinium (atomic number 99) with alpha particles. It was the ninth transuranic element to be synthesized. In 1963, the new element with the atomic number 101 was named mendelevium (Md). Thus, Mendeleev's name became immortal. Mendeleev's genius is also the topic of a YouTube presentation [13].

## Milestones en route to the modern Periodic Table

### 'Electrification' of the Periodic Law

In the period 1904–1924, the electrical composition and structure of the atom was discovered and elucidated. It impacted the Periodic Law in three ways: (1) by replacing atomic mass with atomic number as the independent variable in the Periodic Law, (2) by replacing the empirical concept of valence with the number of outer (or chemically active) electrons in the atom, and (3) by redefining the concept of a chemical element as a class of atomic nuclei having identical nuclear charges.

After the 'electrification' of the Periodic Law three 'mistakes' Mendeleev made, were corrected:

1. The first element is indeed hydrogen, not the hypothesized ether with the atomic mass of about $10^{-7}$ amu.
2. Mendeleev did not believe in the existence of inert gases for a long time, because they fall out of his logic of the Periodic Law. When proofs became very convincing, he reluctantly admitted them by inventing the additional zero group, where the inert gases were placed.
3. The elements Ar (18: 39.948 amu) and K (19: 39.098 amu), Co (27: 58.933 amu) and Ni (28: 58.693 amu) as well as Te (52: 127.60 amu) and I (53: 126.90 amu) were correctly placed in order of the increasing atomic number and not in order of the increasing atomic mass. To the end of his life, Mendeleev was still convinced that there were experimental errors in the determination of their atomic masses.

### Discovery of rare-earth elements

The rare-earth elements, which now constitute the group 3b of the Periodic Table, are scandium, yttrium, lanthanum and the 14 4*f*-elements aka lanthanoids (or lanthanons). The long history of their discovery began in 1794, when the Finnish chemist Johan Gadolin (1760–1852) obtained the yttria earths, and ended in 1948, when the element promethium was found among the products of nuclear fission in an atomic reactor.

All these elements except promethium where obtained from so-called earths (the mixtures of oxides) as a result of long-term and laborious investigations.

Originally, two such earths were isolated. Apart from yttria earths, in 1803 the German chemist Martin Heinrich Klaproth (1743–1817) isolated the ceria earths. Each of them gave birth to several individual rare-earth elements. The history of the discovery of the rare-earth elements is compiled below.

### Ceria earths

- Swedish chemist Carl Gustav Mosander (1797–1858), 1839: $^{58}$Ce
- Carl Gustav Mosander, 1841: $^{57}$La
- Czech chemist Bohuslav Brauner(1855–1935), 1882: $^{59}$Pr
- Austrian scientist Carl Auer von Welsbach (1858–1929), 1885: $^{60}$Nd
- French chemist Paul Émile Lecoq de Boisbaudran (1838–1912), 1880: $^{64}$Gd
- French chemist Eugène-Anatole Demarçay (1852–1903), 1901: $^{62}$Sm, $^{63}$Eu.

### Yttria earths

- Carl Gustav Mosander, 1843: $^{39}$Y
- Swiss chemist Jean Charles Galissard de Marignac (1817–1894), 1886: $^{64}$Gd
- Lecoq de Boisbaudran, 1895: $^{65}$Tb
- Swedish chemist Per Teodor Cleve (1840–1905), 1879: $^{68}$Er, $^{69}$Tu
- Swedish chemist Lars Fredrik Nilson (1840–1899), 1879: $^{21}$Sc
- Lecoq de Boisbaudran, 1886: $^{66}$Dy, $^{67}$Ho
- French chemist Georges Urbain(1872–1938), 1907: $^{70}$Yb
- Carl Auer von Welsbach, 1907: $^{71}$Lu

### Discovery of the Noble Gases

In 1895, the English physicist John William Strutt, 3rd Baron Rayleigh (1842–1919) reported the discovery of a new gaseous element named argon (18) which proved to be chemically inert (noble). This element did not fit any of the known periodic groups. In 1898, the Scottish chemist Sir William Ramsey (1852–1916) suggested that argon be placed into the Periodic Table between chlorine and potassium in a family with helium, despite the fact that the atomic mass of argon was greater than that of potassium. This group

was termed the 'zero' group due to the zero valence of the elements. Sir Ramsey also predicted the future discovery and properties of neon (10). Together with the English chemist Morris William Travers (1872–1961), he discovered the noble gas neon, shortly after their discovery of the element krypton (36) in 1898. Similar to krypton, neon was discovered through the study of liquefied air.

## Atomic structure and the Periodic Table

Although Mendeleev's Periodic Table demonstrated the periodic nature of the elements, it remained for the discoveries of the twentieth century's scientists to explain why the properties of the elements recur periodically.

In 1911, the New Zealander chemist Ernest Rutherford (1871–1937) published studies of the scattering of alpha particles by heavy atom nuclei, which led to the determination of nuclear charge. He demonstrated that the nuclear charge was proportional to the atomic mass of the element. Also in 1911, the Dutch amateur physicist Antonius Johannes van den Broek (1870–1926) proposed that the atomic mass of an element was approximately equal to the 'charge' on the atom. This charge, later termed as atomic number, could be used to number the elements within the Periodic Table. In 1913, the English physicist Henry Gwyn Jeffrey's Moseley (1887–1915) published the results of his measurements of the wavelengths of the X-ray spectral lines of a number of elements. It showed that the ordering of the wavelengths of the X-ray emissions of the elements coincided with the ordering of the elements by atomic number. With the discovery of the elements' isotopes, it became apparent that the atomic mass was not the significant player in the Periodic Law as Mendeleev, Meyer and others had proposed. The properties of an element vary rather periodically with its atomic number.

The question why the Periodic Law exists was answered as scientists developed an understanding of the electronic structure of the elements. It began with the studies of the Danish physicist Niels Henrik David Bohr (1885–1962). Further on, the organization of electrons into shells was explained by quantum mechanics, whose fathers were French physicist Louis-Victor-Pierre-Raymond de Broglie (1892–1997) (wave nature of the electron), Austrian physicist Erwin Rudolf Josef Alexander Schrödinger (1887–1961) (differential equation for the wave of material particle), German physicist and mathematician Max Born (1882–1970) (interpretation of Schrödinger's wave function in terms of probabilities), German theoretical physicist Werner Karl Heisenberg (1901–1976) (uncertainty principle) and Austrian-Swiss-American theoretical physicist Wolfgang Ernst Pauli (1900–1958).

In this new mechanics, the complete characterization of an electron in an atom requires four quantum numbers: $n$, the principal number, $\ell$, the orbital angular momentum quantum number, $m_\ell$, the magnetic quantum number, and $m_s$, the spin quantum number. If two electrons occupy the same orbital, and if their $n$, $\ell$, and $m_\ell$ values are the same, then their $m_s$ values must have different values, namely the opposite half-integer spin numbers $1/2$ and $-1/2$. This so-called Pauli exclusion principle was formulated by Pauli in 1925.

Further milestones were the discovery of the covalent bond and the concept of electron pairs by American physical chemist Gilbert Newton Lewis (1875–1946) as well as the quantum interpretation of the chemical bonding by German physicist Walter Heinrich Heitler (1904–1981) and Jewish–German physicist Fritz Wolfgang London (1900–1954). After these discoveries, the concept of an electron orbital as a part of space, where one can find an electron with a probability no less than 90%, was developed. The orbitals are now commonly depicted in forms of space figures of different symmetry.

## The modern Periodic Table

The family of the 14 $f$-elements, called actinoides, starts with actinium (89), which is the analog of lanthanum (57), and is completed with lawrencium (103). Thorium (90) is the first element where the 5$f$-sublevel should be filled. However, about 70 years ago, the first actinoides were classified as $d$-elements. Therefore, in older chemical textbooks Th (90) is positioned below Hf (72), Pa (91) below Ta (73) and U (92) below W (74). The chemical properties of these pairs of elements are actually very similar. For example, they form stable chemical compounds with oxidation states, corresponding to their group number: $Th^{+4}$, $Pa^{+5}$, $U^{+6}$.

The last major changes to the Periodic Table resulted from the work of the American scientist Glenn Theodore Seaborg (1912–1999) in the middle of the twentieth century. Starting with the discovery of plutonium (94) in 1940, Seaborg and his team synthesized the transuranic elements with atomic numbers from 94 to 102. Seaborg reconfigured the Periodic Table by placing the actinoide series below the lanthanoide series. He was the first who designated these elements as 5$f$-elements (1942). For a long time his 'actinoide hypothesis' was disapproved by the majority of chemists. Seaborg's colleagues even recommended not to publish his findings, because it could 'destroy his scientific reputation'. But Seaborg, being quoted 'I thought that I had no such scientific reputation, which could be destroyed', published his results anyway. It became worldwide accepted only after the synthesis of transuranic elements, especially curium (96) in 1944. These days we know, why the first actinoides are so similar to $d$-elements. At the beginning of the actinoide series the energies of 5$f$- and 6$d$-sublevels are very similar. Actually, the energy of the 5$f$-sublevel of the first actinoides is even higher than the energy of the 6$d$-level.

**Table 2** Suggested periods of discovery of the 118 elements of the Periodic Table

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Elements known to humans since ancient times *(8000 BCE[#]) (Cu)–800 BCE (Sb); 7200 years: 12 elements

Copper (Cu), Lead (Pb), Gold (Au), Silver (Ag), Iron (Fe), Carbon (C), Tin (Sn), Sulfur (S), Mercury (Hg), Zinc (Zn), Arsenic (As), Antimony (Sb)

1669 (P)–1798 (Cr); 130 years: 14 elements

Phosphorus (P), Cobalt (Co), Platinum (Pt), Nickel (Ni), Bismuth (Bi), Hydrogen (H), Oxygen (O), Nitrogen (N), Chlorine (Cl), Manganese (Mn), Molybdenum (Mo), Tellurium (Te), Tungsten (W), Chromium (Cr)

1802 (Ta)–1844 (Ru); 43 years: 28 elements

Tantalum (Ta), Palladium (Pd), Osmium (Os), Iridium (Ir), Rhodium (Rh), Potassium (K), Sodium (Na), Calcium (Ca), Boron (B), Strontium (Sr), Magnesium (Mg), Barium (Ba), Iodine (I), Cadmium (Cd), Selenium (Se), Lithium (Li), Silicon (Si), Zirconium (Zr), Titanium (Ti), Aluminium (Al), Bromine (Br), Beryllium (Be), Vanadium (V)

1861 (Tl)–1898 (Kr/Ne/Xe); 38 years: 24 elements

Thallium (Tl), Rubidium (Rb), Indium (In), Niobium (Nb), Gallium (Ga), Ytterbium (Yb), Holmium (Ho), Thulium (Tm), Scandium (Sc), Samarium (Sm), Erbium (Er), Praseodymium (Pr), Neodymium (Nd), Cesium (Cs), Gadolinium (Gd), Germanium (Ge), Dysprosium (Dy), Fluorine (F), Terbium (Tb), Argon (Ar), Helium (He), Krypton (Kr), Neon (Ne), Xenon (Xe)

1901 (Eu)–1945 (Pr); 45 years: 18 elements

Europium (Eu), Polonium (Po), Radium (Ra), Actinium (Ac), Lutetium (Lu), Ytterbium (Yb), Radon (Rn), Thorium (Th), Rhenium (Re), Hafnium (Hf), Protactinium (Pa), Technetium (Tc), Francium (Fr), Astatine (At), Neptunium (Np), Curium (Cm), Americium (Am), Promethium (Pm)

1949 (Bk)–2010 (Ts/Mc); 62 years: 22 elements

Berkelium (Bk), Californium (Cf), Einsteinium (Es), Fermium (Fm), Mendelevium (Md), Lawrencium (Lr), Nobelium (No), Rutherfordium (Rf), Dubnium (Db), Seaborgium (Sg), Bohrium (Bh), Meitnerium (Mt), Hassium (Hs), Darmstadtium (Ds), Roentgenium (Rg), Copernicium (Cn), Nihonium (Nh), Flerovium (Fl), Livermorium (Lv), Oganesson (Og),Tennessine (Ts), Moscovium (Mc)

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(cf. Sec. 'Early classifications of the chemical elements')

*At that time not understood as elements in the modern definition

[#]BCE (Before Common Era) and BC (Before Christ) mean the same: previous to year 1 CE (Common Era)

Therefore, thorium, protactinium and uranium behave such as $d$-elements. Starting with plutonium (94), the electrons preferably occupy the 5$f$-sublevel and the elements behave such as 'normal' $f$-elements.

For the final confirmation of Seaborg's theory, scientists eagerly expected the nuclear synthesis of element number 104. If Seaborg were right, the 104th element must be the analog of thorium (90) rather than of cerium (58). In the 1960s, small amounts of element 104 were indeed synthesized by Georgy Nikolayevich Flerov (1913–1990) and his team at the Joint Institute for Nuclear Research in Dubna/Soviet Union and independently by Albert Ghiorso (1915–2010) and colleagues at Lawrence Berkeley National Laboratory in California/USA. The new element was made by bombarding $^{242}$Pu with accelerated neon ions (Dubna) and by bombarding $^{249}$Cf with accelerated carbon ions (Berkeley). The priority of the discovery and, therefore, the naming of the element was disputed between Soviet and American scientists, and it was not until 1997 that the International Union of Pure and Applied Chemistry (IUPAC) established rutherfordium as the official name for element 104, named after Ernest Rutherford (cf. section 'Atomic structure and the Periodic Table').

The first experiments resulted in less than 40 atoms of rutherfordium with half-lives from 70 s to 11 min. The Czech chemist Ivo Zvára (1934–living) was among the main 'heroes' in Dubna. He developed very sophisticated methods for the investigation of such extremely small amounts of substances. He determined significant differences of the properties of rutherfordium compared to those of the preceding elements. For example, such as hafnium (72), rutherfordium forms the volatile tetrachloride $RfCl_4$, while the chlorides of the preceding actinoides are solid substances with boiling points near 1500 °C. Thus, the actinoide series ended with element 103, as Seaborg had predicted.

In 2016, the IUPAC confirmed and officially named the newly discovered elements nihonium (Nh), moscovium (Mc), tennessine (Ts), and oganesson (Og). Thereby, 118 elements from hydrogen to oganesson have been discovered or synthesized. The first 94 elements exist naturally, while the elements with atomic numbers from 95 to 118 have only been synthesized in laboratories or nuclear reactors. Table 2 presents suggested periods of discovery of the 118 elements known to date. In each group the elements are arranged based on the year of their discovery. Regarding the names and symbols of the chemical elements, we follow the decisions made by IUPAC. In the past, the names of several elements have been the subject of controversies until IUPAC established an official name. In most cases the controversy was due to a priority dispute as to who first found conclusive evidence for the existence of an element, or as to what evidence was in fact conclusive.

**Fig. 3** Short-form Periodic Table



The nuclear synthesis of heavy transuranic elements is going on. In Dubna the generation of elements 119 and 120 is being pursued [14]. Scientists expect that beyond element 120 relatively stable far-transuranic elements should exist. The reasoning for such expectation is substantiated by the so-called 'shell model' of the atomic nucleus. According to this model, the elements with atomic numbers 2 (He), 8 (O), 14 (Si), 20 (Ca), 28 (Ni), 50 (Sn) and 126 realize very stable nuclei. Who would doubt that this is correct for the first six elements! Could, however, an element with the atomic number 126 exist and what would be its chemical properties? We hardly ever have an answer to these questions. According to the $(n+\ell)$ rule[2], the $g$-sublevel should be filled (electronic formula $8s^2 5g^6$). There are, however, reasonable doubts that such an element would be stable, even if it could be synthesized. Due to the nuclear reaction known as K-capture[3], the stability of the nucleus does not guarantee the stability of the atom as a whole.

On 20 December 2017, during its 74th Plenary Meeting, the United Nations General Assembly 72nd Session has proclaimed 2019 as the International Year of the Periodic Table of Chemical Elements [15] (IYPT 2019). In proclaiming an International Year focusing on the Periodic Table of Chemical Elements and its applications, the UN has recognized the importance of raising global awareness of how chemistry promotes sustainable development and provides solutions to global challenges in energy, education, agriculture and health. This International Year brings together many different stakeholders including UNESCO, scientific societies and unions, educational and research institutions, technology platforms, non-profit organizations and private sector partners to promote and celebrate the significance of the Periodic Table and its applications to society. IYPT 2019 coincides with the 150th anniversary of the discovery of the Periodic Law by Dmitri Ivanovich Mendeleev in 1869.

## The short-form Periodic Table

The existing literature about various aspects of the Periodic Table is enormous. Over time, an immense variety of graphic presentations of the Periodic Table has been published, cf. e.g. [16]. In addition, attractive interactive diagrams offer an easy access to a plethora of information, cf. e.g. [17–21].

The oldest version of the Periodic Table is the short-form Table (Fig. 3), originated during Mendeleev's

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[2] Orbitals which have the least value of $(n+\ell)$ will be filled first with electrons. If there are two orbitals that have the same value of $(n+\ell)$, then the orbital that has the least value of '$n$' will be filled first. '$n$' is the principal quantum number and '$\ell$' the orbital angular momentum quantum number.

[3] The nucleus of a heavy element captures the inner electron, one of the protons transforms to a neutron and the atomic number is reduced by one.

**Fig. 4** Detailed version of the short-form Periodic Table



**Fig. 5** Long-form Periodic Table



lifetime. It includes eight columns (groups). The chemical elements in main groups 'a' and side groups 'b' possess similar electronic configurations on the outer electronic energy levels, which allows the search for analogies in their chemical behavior. Such type of presentation is still successfully used at many universities of the former Soviet Union.

In the versions that are used particularly at Ukrainian universities, group 0 is represented as main group 'a' of group VIII, whereas the triads of *d*-elements inhabit the side group 'b', as shown in Fig. 4.

According to the recommendations of IUPAC [22], most universities around the world use the long-form Periodic Table, which includes 18 groups without subgroups (Fig. 5).

**Table 3** Selected similarities of chemical properties in main group 'a' and side group 'b'

| Group IV | $SiO_2$, $TiO_2$ and $ZrO_2$ constitute inert refractory oxides with atomic lattices |
|---|---|
| | Hexafluorosilicates and hexafluorotitanates of alkali and alkaline earth metals possess very similar properties (e.g. melting point, pattern of thermal decomposition) |
| | The phase diagrams with alkali metal fluorides are almost identical |
| Group V | Both phosphorus and vanadium form polyoxometalates |
| | Crystals of polyphosphates and polyvanadates exhibit similar structures |
| Group VI | Comparable polysulfuric and polychromic acids |
| Group VII | Crystals of perchlorates $M^{+1}ClO_4$ and permanganates $M^{+1}MnO_4$ are isomorphous |
| | Their solid solution cannot be separated by recrystallization |

From the viewpoint of analogies in electronic configurations of the chemical elements, the long-form Periodic Table appears to be more logical than the short-form presentation. The electronic structure of the outer shells in all groups seems to be similar, if we disregard the electronic structures of the inner level (see below). However, some analogies are lost in this type of Table, namely the analogies in the electronic structures (and thus, in the properties) of the chemical elements of both subgroups when these elements realize the highest possible oxidation state. Selected similarities of chemical properties in the main group 'a' and side group 'b' of groups IV–VII are listed in Table 3.

Therefore, we shall use the short-form Table to find similarities and differences in the chemical behavior of elements based on the similarities and differences of the structure of valence (outer) electronic shells.

## Full, close and approximate electronic analogies

Evidently, similarities in chemical properties of chemical elements are determined by similarities in the structure of the atoms' outer electronic shells. Analogous elements can be found inside each group of the Periodic Table. However, a thorough consideration leads to the conclusion that within such analogies some peculiarities exist. These characteristics result not exclusively from the features of the valence shells, but also from the character of the inner electrons beneath the electronic valence level.

Obviously, the elements of group Ia constitute full analogs. Their single valence electron $ns^1$ is located above the completely filled electronic shells of the corresponding inert (noble) gas: Li [He]$2s^1$, Na [Ne]$3s^1$, K [Ar]$4s^1$, Rb [Kr]$5s^1$, Cs [Xe]$6s^1$. As a result, the properties of the alkali metals change gradually. Their chemical activity increases as the atomic number rises.

One could assume that the same pattern would be observed in a series of $2s$-elements, which have a similar electronic configuration, namely [noble gas]$ns^2$. If we consider, however, the electronic configurations of their excited state with unpaired electrons, we notice some distinction between beryllium Be* [He]$2s^1 2p^1$ and magnesium Mg* [Ne]$3s^1 3p^1$. The difference results from the character of the

$p$-electron. In the excited Be* atom it occupies the 2nd electronic level, whereas in Mg* it is allocated on the 3rd level. The $2p$-sublevel is the first one; there are not any shielding $p$-electrons at a lower level. In the Russian chemical literature such newly emerged sublevels ($1s$, $2p$, $3d$, $4f$) are called kainosymmetric, from the Greek word καινούργιος (kainoúrgios), which means new. This approach is helpful to understand the analogies of the chemical behavior of elements.

The electrons on kainosymmetric sublevels are not shielded by inner electrons and, therefore, cannot be easily removed. That is the reason why the metallic properties of elements with the valence electrons on kainosymmetric orbitals are diminished [23, 24]. Consequently, beryllium's metallic character is less pronounced than that of magnesium, and its hydroxide is amphoteric. We define the analogy between Be and Mg as close, but not as full analogy. On the other hand, the metals from magnesium to barium are full analogs, and their properties vary gradually as the atomic numbers increase.

The pattern becomes more complicated when we examine electronic analogies in groups containing $p$-elements. It is obvious that the electronic structures of elements of main groups $\{ns^2 np^{N-2}\}$ differ from those of side groups $\{ns^2 (n-1)d^{N-2}\}$, because the behavior of $p$- and $d$-electrons in a chemical bond varies significantly. Therefore, similarities in chemical properties can be observed only in the case, when all outer electrons are lost. Such compounds contain the elements in their highest oxidation state, which is equal to the group number $N$. This level of analogy can be characterized as approximate.

In subgroups, both main and side, the analogies are not always on a full level. As an example, we compare the electronic configuration of the $p$-elements of the 2nd ($2s^2 2p^{N-2}$) and 3rd ($3s^2 3p^{N-2} 3d^0$) periods. First, the elements of the 2nd period have no empty $d$-orbital in the outer electronic level. Therefore, unpairing and promotion of the valence electrons onto this level to form a chemical bond is impossible. Second, the $p$-sublevel of the elements of the 2nd period is kainosymmetric.

The elements of the 3rd and 4th periods could be assumed as full electron analogs. However, this is not the

**Table 4** Electronic analogies in groups IV–VII

| Group/ Period | IV | V | VI | VII |
|---|---|---|---|---|
| 2 | $C_{([He]2s^22p^2)}$ | $N_{([He]2s^22p^3)}$ | $O_{([He]2s^22p^4)}$ | $F_{([He]2s^22p^5)}$ |
| 3 | $Si_{([Ne]3s^23p^2)}$ | $P_{([Ne]3s^23p^3)}$ | $S_{([Ne]3s^23p^4)}$ | $Cl_{([Ne]3s^23p^5)}$ |
| 4 | $Ti_{([Ar]4s^23d^2)}$ $Ge_{(3d^{10}4s^24p^2)}$ | $V_{([Ar]4s^23d^3)}$ $As_{(3d^{10}4s^24p^3)}$ | $Cr_{([Ar]4s^13d^5)}$ $Se_{(3d^{10}4s^24p^4)}$ | $Mn_{([Ar]4s^23d^5)}$ $Br_{(3d^{10}4s^24p^5)}$ |
| 5 | $Zr_{([Kr]5s^24d^2)}$ $Sn_{(4d^{10}5s^25p^2)}$ | $Nb_{([Kr]5s^24d^3)}$ $Sb_{(4d^{10}5s^25p^3)}$ | $Mo_{([Kr]5s^24d^4)}$ $Te_{(4d^{10}5s^25p^4)}$ | $Tc_{([Kr]5s^24d^5)}$ $I_{(4d^{10}5s^25p^5)}$ |
| 6 | $Hf_{(4f^{14}6s^25d^2)}$ $Pb_{(5d^{10}6s^26p^2)}$ | $Ta_{(4f^{14}6s^25d^3)}$ $Bi_{(5d^{10}6s^26p^3)}$ | $W_{(4f^{14}6s^25d^4)}$ $Po_{(5d^{10}6s^26p^4)}$ | $Re_{(4f^{14}6s^25d^5)}$ $At_{(5d^{10}6s^26p^5)}$ |

case, because the inner electrons below the outer shell are different. The elements of the 3rd period are characterized by the completely filled electronic shell of the noble gas neon, whereas the elements of the 4th period possess a filled sublevel $3d^{10}$. These subtle peculiarities in the electronic structures substantiate certain differences in the chemical behavior of $p$-elements in the particular groups of the Periodic Table. Thus, the full electronic analogy between $p$-elements is observed only for the last triads of each group: Ga–In–Tl, Ge–Sn–Pb, As–Sb–Bi, Se–Te–Po and Br–I–At. It is worthwhile to note that there are certain property differences in these triads, due to additional factors which will be discussed below. Table 4 illustrates the character of electronic analogies among the elements in groups IV–VII. Full lines correspond to full, dashed to close and dotted to approximate analogies. The analogies between each of the three $d$-elements in the side subgroups are only close, not full. It will be clear after analyzing their electronic configurations taking into account the character of both the outer valence electrons and the electrons beneath. Thus, $d$-elements of the 4th and 5th periods (Ti–Zr, V–Nb, Cr–Mo, Mn–Tc) possess completely filled subshells of the inert (noble) gases argon and krypton. However, the $3d$-electrons of the elements of the 4th period are kainosymmetric, while the $4d$-electrons are not. Therefore, $4d$-elements (5th period) can easily loose all their $d$-electrons to form stable compounds with their highest oxidation states ($Zr^{+4}$, $Nb^{+5}$, $Mo^{+6}$, $Tc^{+7}$). The $3d$-elements (4th period), on the other hand, form a variety of relatively stable compounds with intermediate oxidation states ($Ti^{+3,+2}$, $V^{+4,+3,+2}$, $Cr^{+3}$, $Mn^{+6,+4,+2}$). The 14 $5d$-lanthanoide elements (6th period) contain a completed $4f^{14}$ subshell beneath the valence electron shell. As a result, their chemical properties vary only to a minor extent with increasing atomic number.

Based on the short form of the Periodic Table, we have described group analogies. We are convinced that such approach is very helpful for learning the basics of inorganic chemistry, especially for freshman students. In the closing section, we will answer some questions which are often asked.

## Questions and answers

*Q1* Why are the chemical properties of hydrogen ($1s^1$) very different from those of alkali metals ($ns^1$)?

*Q2* What are the characteristics of the chemical behavior of $p$-elements of the 2nd period?

*Q3* Why are the $p$-elements of the 4th period in their highest oxidation states often reluctant to form chemical compounds? Why are such compounds rather strong oxidizing agents?

*Q4* Why do $p$-elements of the 6th period easily form compounds, which contain the elements in the oxidation state $+(N–2)$, but compounds containing the same elements with an oxidation state $+ N$ are usually less stable ($N$ represents the group number)?

*Q5* Why are the properties of *d*-elements of the 6th period very similar to those of the elements of the preceding 5th period?

*A1* The single electron of hydrogen is located on the kainosymmetric 1*s*-sublevel. Therefore, it cannot be easily removed. Besides, one more electron can be added to the 1*s*-orbital to form the hydride ion H$^-$ with the electronic configuration of the inert gas helium.

The single valence electron ns$^1$ of alkali metals is shielded by the inner *s*-electrons and is much more distant from the nucleus. Therefore, all *s*-elements of group I are active metals while hydrogen behaves such as a nonmetal.

*A2* The *p*-electrons of these elements are on the kainosymmetric 2*p*-sublevel, and thus cannot be easily removed. Because of that they are much more active nonmetals in comparison to the *p*-elements of the 3rd period. In addition, there are no vacant *d*-orbitals on the 2nd electronic level, which restricts their possibilities for chemical bonding. According to the number of orbitals on the 2nd level, these elements can form no more than four chemical bonds.

*A3* The compounds of 4th period's arsenic, selenium and bromine have the tendency to be unstable in their maximum oxidation states. Here are three examples:

Arsenic pentachloride, $AsCl_5$, which was first prepared as recently as 1976, decomposes at around $-50\,°C$, while $PCl_5$ and $SbCl_5$ are quite stable. Perbromates $M^{+1}BrO_4$ were first synthesized only in the 1960s by the reaction of bromates with the just discovered xenon fluorides. They are much stronger oxidants than perchlorates and periodates. Selenic acid, $H_2SeO_4$, can oxidize even gold, while sulfuric acid, $H_2SO_4$, and telluric acid, $H_6TeO_6$, cannot.

The reason for these 'abnormalities' is an effect called d-constriction. The electrons on the kainosymmetric 3*d*-orbitals are poorly shielded by inner electrons and strongly attracted to the atom nucleus. Along the 4th period the nuclear charge increases and the atomic diameter shrinks. As a result of the filled $3d^{10}$-sublevel the atomic radii of the elements of the 3rd and 4th periods differ only slightly, while the atomic number increases from potassium (19) to krypton (36) by 18 units. The valence electrons of the 4th period's elements are difficult to remove and their maximum oxidation states become unstable.

*A4* As an example, we will discuss the properties of the p-metals thallium, lead and bismuth with electronic configurations $6s^26p^1$, $6s^26p^2$ and $6s^26p^3$, respectively. These metals easily form the cations $Tl^+$, $Pb^{2+}$, $Bi^{3+}$, but are very reluctant to form compounds with oxidation states $+3$, $+4$ and $+5$, which are oxidizers. The more stable lower oxidation states correspond to the electronic configuration $6s^26p^0$. That is, only the available *p*-electrons are lost while the electron pair $6s^2$ remains. Therefore, such phenomenon is sometimes called 'the inert pair effect'. This effect is the result of submersion of the pair of *s*-electrons inside the atom's electronic shells. Such a 'dived' electronic pair becomes unavailable or at least hardly available for the formation of chemical bonds.

At present, no generally accepted explanation for this phenomenon exists. The most probable cause is the shrinkage of the *s*-sublevels, due to the relativistic effects resulting from very high velocities of the innermost *s*-electrons near the nucleus of heavy elements. As follows from the theory [23], these electrons in atoms with atomic numbers $Z \geq 60$ are moving with velocities close to the light velocity, whereupon their velocity increases proportionally to $Z^2$. The relativistic masses of such electrons become much bigger than the rest masses. The distance to the nucleus, which can be expressed as Bohr radius, is inversely proportional to the electron mass:

$$a_o = \frac{h^2}{4\pi^2 mZe^2}$$

where *h* is Planck's constant, *m* the electron mass, *Z* the atomic number and *e* the electron charge.

The relativistic increase of the electron mass results in constriction of 1*s*-orbitals and in decrease of all subsequent *s*-orbitals.

*A5* The properties of pairs such as Zr–Hf, Nb–Ta and Mo–W are almost identical. This results from the so-called lanthanoide contraction or *f*-contraction. The nature of this effect is similar to the effect of *d*-constriction (cf. *A3*).

The electrons beneath the outer level in atoms of 5*d*-elements (6th period) do not exhibit the completed shell of a noble gas, as the atoms of 4*d*-elements (5th period) do. In fact, they are characterized by the fully filled $4f^{14}$-sublevel. The shrinkage of the kainosymmetrical 4*f*-orbitals proceeds, as the outer shell is being filled with *d*-electrons. As a result, the atomic radii of 4*d*- and 5*d*-elements are virtually the same. Therefore, the properties of the above mentioned pairs are almost identical.

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