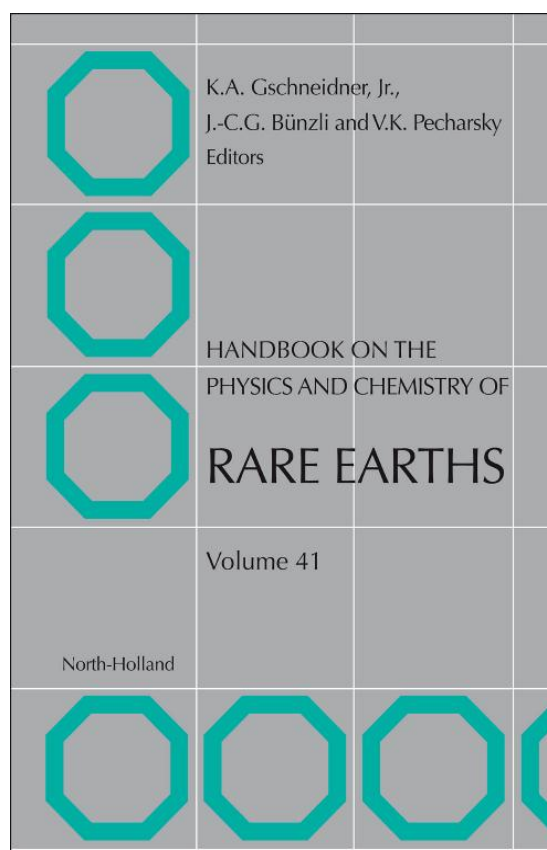


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CHAPTER **248**

Accommodation of the Rare Earths in the Periodic Table: A Historical Analysis

Pieter Thyssen and **Koen Binnemans**

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Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, P.O. Box 2404, Heverlee, Belgium

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List of Symbols and Acronyms

AW	atomic weight
EW	equivalent weight
G	group number
<i>l</i>	angular momentum quantum number
<i>n</i>	principal quantum number
S	series number
X	general element symbol
Z	atomic number

1. INTRODUCTION

The *Periodic System of the Elements*, also known as the *Periodic Table*, represents the cornerstone of modern chemistry because it creates order in the multitude of chemical elements and because it allows the prediction of trends in the chemical properties of the elements (Mazurs, 1974; Puddephatt and Monaghan, 1985; Quam and Battell-Quam, 1934a,b,c; Scerri, 2007; Stewart, 2007; van Spronsen, 1969; Venable, 1896; Wang and Schwarz, 2009). Nearly every textbook of inorganic chemistry contains a graphical representation of the periodic system. Poster versions of the periodic table can be found on the walls of many classrooms and lecture halls. This gives the impression that the shape of the periodic system and the position of the individual elements has been fixed since it was introduced for the first time to the community of chemists by Dmitrii Ivanovich Mendeleev in 1869, and that the only changes are the insertion of newly discovered elements. This impression is wrong. Since Mendeleev's discovery of the periodic law, the periodic system of chemical elements has undergone a strong evolution. Even at present, different standard forms of the periodic table are in use. The most striking differences can be found in group IIIB (group 3) which consists according to some periodic tables of Sc, Y, La, and Ac, whereas this is Sc, Y, Lu, Lr according to other tables, while in still other periodic tables the whole series of the lanthanides and actinides are accommodated in this group. Other topics of discussion are the placement of H, He, Al and the labeling of the element group {Zn, Cd, Hg} as transition metals or not (Bent, 2006; Cronyn, 2003; Habashi, 1997; Jensen, 2003, 2008a; Laing, 2007; Novaro, 2008; Scerri, 2005). Besides the standard forms of the periodic table, hundreds of different varieties have been proposed, including spiral, helical, circular and three-dimensional models (Mazurs, 1974).

The fact that there is still an ongoing debate on the question which elements have to be placed in group IIIB indicates that the accommodation (or placement) of the rare earths in the periodic table has always been a difficult issue. The similarities in their chemical properties and the small differences in atomic weight when going from one element to the next one, have caused many troubles to the earlier investigators of the periodic system (Akeroyd, 2003). Nilson and Pettersson (1880) stated: "The periodic table possesses insurmountable difficulties with the rare earth elements." The problem of the accommodation of the rare earths in the periodic table was complicated even more by assuming wrong values for the valency and atomic weights of these elements. One could also think that the accommodation of the rare earths in the periodic table was difficult because only a few rare earths were known at the time of Mendeleev's seminal work of 1869. From a retrospective point of view however, the classification of the chemical elements would have been next to impossible if all the rare-earth elements had been known at that time (Spronsen, 1969).

While the history of the discovery and the separation of the rare earths is well documented, the story of the accommodation of the rare earths in the periodic table is less well known. Part of the story can be found in the famous book on the periodic system of van Spronsen (1969), but recent investigations in the field of the history and philosophy of chemistry have shed new light on the early episodes of the development of the periodic system after 1869. Moreover, the accommodation of the rare earths in the periodic table is still an active research topic. In 2008 and 2009, there was a debate in the *Journal of Chemical Education* on the position of the lanthanides and actinides in the periodic table (Clark and White, 2008; Lavelle, 2008a,b, 2009; Stewart, 2008; Jensen, 2008b, 2009; Clark, 2008; Scerri, 2009a; Laing, 2009).

The aim of this chapter is to give an overview of the evolution of the position of the rare earths in the periodic table, from Mendeleev's time to the present. It will be shown that three fundamentally different accommodation methodologies have been proposed over the years. Mendeleev considered the rare-earth elements as homologues of the other elements and placed them throughout the system in all different groups from I to VIII. Other chemists looked upon the rare earths as forming a special intraperiodic group and they collectively clustered the rare-earth elements in one of the groups of the periodic table. Still others adhered to the so-called intergroup accommodation of the rare earths, according to which the rare-earth elements do not show any relationship with other elements, so that they had to be placed within the periodic table as a separate family of elements, completely unconnected to the other groups. This was accomplished by accommodating the rare earths in between two groups of the periodic system. The rare-earth elements

thus showed some analogy with the transition metals (according to Mendeleev's definition) in the sense that both types of elements were separated from the rest of the system and that both formed a transition between the two main groups of Mendeleev's system. The intergroup accommodation became the preferred one in the twentieth century, because it was in agreement with Bohr's quantum model of the atom. The contributions of Dmitrii Mendeleev, Bohuslav Brauner, Sir William Crookes, Henry Moseley, Niels Bohr, and Glen Seaborg will be put into a historical context. The advantages and disadvantages of the different representations of the modern periodic table, including the left-step periodic table, will be discussed. Special attention will be paid to the question whether lanthanum (actinium) or rather lutetium (lawrencium) should be located below yttrium in the periodic table. Although it would be scientifically more correct to use the term *relative atomic mass*, the historical term *atomic weight* will be used throughout this chapter. We will use the numbering IIIB (US system) for the group containing scandium and yttrium. This group has been numbered 3 in the more recent IUPAC system and IIIA in the European system.

2. A SHORT HISTORY OF THE DISCOVERY OF THE RARE-EARTH ELEMENTS

In this section of the chapter, a brief account of the fascinating history of the discovery of the rare-earth elements will be given. More detailed information can be found in the works of Weeks (1956), Evans (1996), Niinistö (1997) and in Chapter 73 of this Handbook (Szabadváry, 1988). The story began in 1787, when Carl Axel Arrhenius (1757–1824), a lieutenant of the Swedish army and an amateur mineral collector, went on a trip near the small village of Ytterby on the island of Resarö close to Vaxholm (east of Stockholm) and discovered a heavy black mineral in a feldspar quarry. At first sight, the mineral he later called "black stone" resembled asphalt or coal, but it had a remarkably high mass density. Arrhenius' black mineral was first described in the literature by Bengt Reinhold Geijer (1758–1815), who incorrectly assumed that the heavy mineral contained the newly discovered element tungsten (wolfram). In 1794, Johan Gadolin (1760–1852), a Finnish professor of chemistry and mineralogy in the town of Åbo (now Turku), analyzed a sample of the black mineral given to him by Arrhenius, and he succeeded in isolating a new earth (i.e., a metal oxide) which he subsequently named "Ytterby earth." The unknown white earth had some properties that were reminiscent of alumina, while other properties were more similar to those of calcium oxide. Gadolin's work was published in 1796. His discovery was confirmed a year later by the Swedish chemist Anders Gustav Ekeberg (1767–1813), who analyzed a larger sample. Ekeberg renamed Gadolin's

new earth “yttria” and proposed the name *gadolinite* for the black mineral discovered by Arrhenius, in honor of Gadolin. Back in 1751, the Swedish chemist Axel Frederik Cronstedt (1722–1765), had discovered a heavy stone in the Bastnäs mine in Sweden. Cronstedt’s colleague Tobern Bergman (1735–1784) thought it contained an unknown earth, but it was not until 1803 that Martin Heinrich Klaproth (1743–1817) and Jöns Jacob Berzelius (1779–1848), together with Wilhelm Hisinger (1766–1852), independently isolated a rare-earth element. Klaproth called it “terre ochroite,” because it formed colored salts with acids. Berzelius and Hisinger named it “ceria” after the newly discovered asteroid Ceres, and “ceria” became the name preferred by chemists. Therefore, at the beginning of the nineteenth century two rare-earth elements were known: “yttria” (discovered in 1794) and “ceria” (discovered in 1803). However, both “elements” turned out to be complex mixtures later on. In [Figures 1 and 2](#) the chronology of the splitting of “ceria” and “yttria” in the different rare-earth elements is illustrated.

The pronounced similarity between the chemical and physical properties of the rare-earth elements made their isolation a difficult task. The traditional methods of chemical analysis were to no avail and chemists of

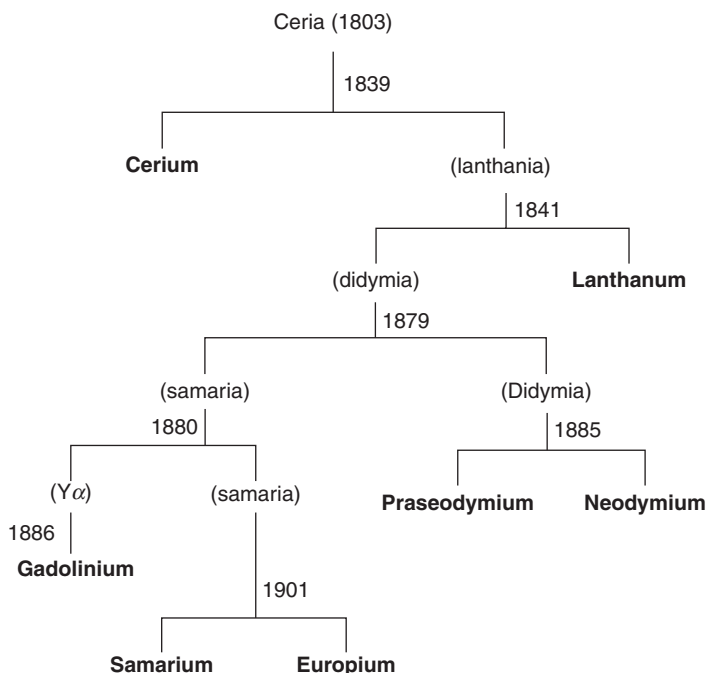


FIGURE 1 Chronology of the splitting of “ceria” in the different composing rare-earth elements.

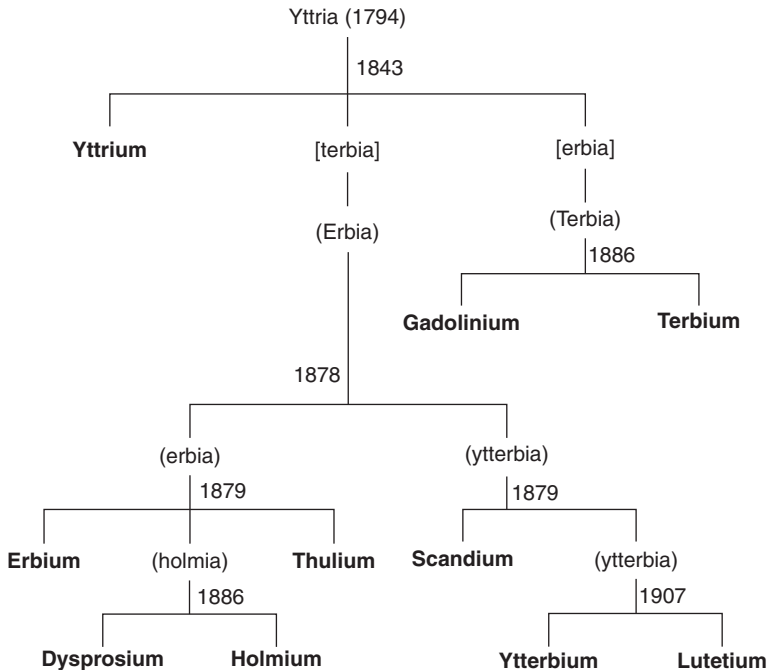


FIGURE 2 Chronology of the splitting of “yttria” in the different composing rare-earth elements.

the early nineteenth century felt obliged to turn to the processes of chemical fractionation (fractional crystallization or fractional precipitation), exploiting the very small differences in the solubility of the rare-earth salts. The number of crystallization steps usually amounted to several thousands, if not tens of thousands. The tedious monotony and dreariness of the exhaustive fractionations is reflected in some of the names of the rare-earth elements. Thus, the Greek origin of lanthanum (La), *λανθάνειν* (*lanthanein*), means “to lie hidden.” Dysprosium (Dy) on the other hand is named after the Greek *dysprositos*, which means that it was “hard to get.” Finally thulium (Tm) refers to its Latin origin, *Thule*, “the farthest northernmost fringe of the civilized world (Evans, 1996).”

It was one of Berzelius’ assistants and the curator of the mineral collections of the Stockholm Academy of Sciences, Carl Gustaf Mosander (1797–1858), who demonstrated the complexity of both “yttria” and “ceria.” When Mosander heated some “cerium” nitrate in 1839, the salt partly decomposed, and on a treatment with dilute nitric acid, he succeeded in extracting a new earth. He called the new element lanthanum (German: Lanthan) and its oxide “lanthana.” Mosander retained the old name *ceria* (Ce) for the insoluble portion of the “ceric” oxide in nitric acid.

In 1841, Mosander discovered another rare earth, “didymium” (Di), in ceria. Unfortunately, “didymium” did not prove to be a genuine element, and it was shown later on that didymium could be separated in two other elements, neodymium and praseodymium (*vide infra*). Having demonstrated the complexity of “ceria” by the identification of at least three elements—cerium, lanthanum, and didymium—Mosander now moved over to his experimental investigations of “yttria” (gadolinite). At the beginning of 1843, Mosander succeeded in splitting his samples of gadolinite in at least three fractions by means of fractional precipitation with ammonium hydroxide. He kept the name *yttria* for the colorless fraction, and named the yellow and rose colored earths “erbia” (Er) and “terbia” (Tb), respectively. The names “erbia” and “terbia” were later interchanged for some obscure reasons and this of course led to confusion among inorganic chemists. The rare-earth story could be briefly recapitulated by noting that “ceria” had been split in cerium, lanthanum and “didymium,” whereas “yttria” had been split in yttrium, “erbi-um,” and terbi-um. During the following 35 years (from 1843 to 1878), no new elements were added to the list of rare earths. Thus when Mendeleev introduced his periodic table in 1869, six rare earths were known: yttrium, lanthanum, cerium, “didymium,” “erbi-um” and terbi-um.

During the second half of the nineteenth century, a number of rare-earth specialists started applying the various spectroscopic techniques which had been developed by Robert Wilhelm Bunsen (1811–1899) and Gustav Kirchhoff (1824–1887) back in the 1860s in Heidelberg, Germany. Although this new experimental tool proved to be indispensable for the discovery of new elements, it also led to erroneous results. The complexity of absorption and emission spectra, spark spectra and phosphorescent spectra often resulted in wrong interpretations of spectral lines. The combined action of chemical analysis and physical spectroscopy sparked off a multitude of claims and counterclaims for discoveries of new chemical elements, but no one knew how to judge the worth of these assertions. This caused the number of rare-earth elements described in the literature to grow steadily. The chemical community thus witnessed the appearance and disappearance of columbium, damarium, decipium, demonium, euxenium, incognitum, mosandrum, philippium, rogerium, and victorium, to name just a few examples. Fortunately, spectroscopy also aided in discovering a number of genuine rare-earth elements.

The Swiss chemist Jean Charles Galissard de Marignac (1817–1894), was the first in applying these spectroscopic methods. He was 23 years old when he embarked upon his quest for new rare-earth elements. He demonstrated in 1878 that “erbia” was a complex mixture of at least two rare-earth elements, erbi-um and “ytterbi-um” (Yb), by heating “erbi-um” nitrate and extracting the decomposed salt with water. The little Swedish village Ytterby thus holds a distinguished place in the history of the rare-earth elements.

Four rare-earth elements (yttrium, ytterbium, erbium, and terbium) have been named in honor of this village. A year later, the Swedish chemist Lars Fredrik Nilson (1840–1899), discovered another element in “erbia” and he named it *scandium* (Sc) in honor of Scandinavia. At the same time, Nilson’s compatriot, the geologist and chemist Per Theodor Cleve (1840–1905) succeeded in resolving the “erbia” earths yet another step further, when he separated it into three components: erbium, “holmium” (Ho) and thulium (Tm). The name “holmium” refers to Stockholm (Cleve’s native city) and had been independently discovered by the Swiss chemists Marc Delafontaine (1838–1911) and Jacques-Louis Soret (1827–1890), who had coined the metal element X on the basis of its absorption spectrum.

Marignac had been one of the first chemists to question the elemental character of Mosander’s “didymium” back in 1853. It took a quarter of a century before Delafontaine started observing some mysterious variations in the spectra of “didymium.” He thus noted the appearance of two new lines and took it as an indication for the existence of a new element, which he called “decipium” from the Latin “to deceive” or “to stupefy.” However, Paul-Emile Lecoq de Boisbaudran (1838–1912), another specialist in spectroscopic analysis, revealed the real identity of “decipium” in 1879 and he showed it to consist of a mixture of known rare earths. His spectroscopic investigations aided him in the resolution of “didymium” when he isolated “samarium” (Sm) from the mineral samarskite over the course of that same year. Didymium completely ceased to exist in 1885 when Carl Auer von Welsbach (1858–1929) succeeded in splitting it in two fractions, a green fraction which he named *praseodymium* (Pr, from the Greek for “green twin”) and a pink one which he had named *neodymium* (Nd, from the Greek for “new twin”).

Lecoq de Boisbaudran further resolved “samarium” in 1886 in genuine samarium and another rare-earth element which appeared identical with Marignac’s $Y\alpha$, isolated in 1880. Marignac and Lecoq de Boisbaudran decided to name this element *gadolinium* (Gd) after the mineral gadolinite. *Dysprosium* (Dy) was discovered during the same year. *Europium* (Eu) was discovered in 1901 by Eugène-Anatole Demarçay (1852–1904) who was a specialist in spectroscopy. The story about the discovery of lutetium (Lu) and promethium (Pm) will be discussed in [Sections 5.3 and 5.4](#).

3. DMITRII IVANOVICH MENDELEEV

3.1 Mendeleev’s Attempted System

On February 17, 1869 (according to the old Julian calendar), the Russian chemist Dmitrii Ivanovich Mendeleev (1834–1907, [Figure 3](#)) wrote a pamphlet entitled “An Attempted System of the Elements Based on



FIGURE 3 Dmitrii Ivanovich Mendeleev (1834–1907). Photo and permission from Edgar Fahs Smith Collection.

Their Atomic Weights and Chemical Analogies” in both the Russian and the French language (Figure 4) (Mendeleev, 1869a). The whole set of chemical elements known at that time had been logically classified in six columns of increasing atomic weight (or relative atomic mass) and 19 rows of natural groups, thus representing the first embodiment of the periodic law and the first version of the periodic table (Gordin, 2004; Kolodkine, 1963; Mendeleev, 1889; Pissarjevski, 1955). By sending the *Attempted System* right away (the actual discovery had been made on the same day), Mendeleev ensured the priority of his discovery. When inspecting Mendeleev’s *Attempted System* in more detail, one can notice an intriguing fact. In general, when reading from top to bottom and from left to right, one should obtain an ever increasing atomic weight sequence. However, this sequence gets interrupted four times. First, when passing from indium (In, 75.6, third column, bottom row) to titanium (Ti, 50, fourth column, top row), and a second time when moving from thorium (Th, 118, fourth column, bottom row) to zirconium (Zr, 90, fifth column, top row). The atomic weight sequence is violated twice more by the inversion of tellurium (Te) and iodine (I), and by the insertion of gold (Au) and bismuth (Bi). The only possible way of restoring the sequence of the In–Ti and the Th–Zr violations would be by eliminating a total of seven elements from the system, namely yttrium (Yt), indium (In), cerium (Ce), lanthanum (La), didymium (Di), erbium (Er) and thorium (Th).

ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

		Ti = 50	Zr = 90	? = 180.
		V = 51	Nb = 94	Ta = 182.
		Cr = 52	Mo = 96	W = 186.
		Mn = 55	Rh = 104,4	Pt = 197,1.
		Fe = 56	Rn = 104,4	Ir = 198.
		Ni = Co = 59	Pl = 106,8	O = 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
		Ca = 40	Sr = 87,6	Ba = 137
		? = 45	Ce = 92	Pb = 207.
		?Er = 56	La = 94	
		?Yt = 60	Di = 95	
		?In = 75,6	Th = 118?	

Д. Менделѣевъ

FIGURE 4 An attempted system of the elements based on their atomic weight and chemical analogies. A pamphlet with Mendeleev's first periodic system, distributed on February 17, 1869.

Indeed, if that were the case, the sequence would have passed from the unknown element with an atomic weight of 45 to titanium with an atomic weight of 50, and from strontium with an atomic weight of 87.6 to zirconium with an atomic weight of 90, completely in accordance with the gradual increase in atomic weight. It must be noted that terbium was already known at the time of the first version of the periodic table in 1869, but Mendeleev decided not to include this element in his table, following Bunsen's and Bahr's advice. Nonetheless, all other known rare-earth elements were clearly present in Mendeleev's *Attempted System*, but none of them had been correctly accommodated. Moreover, the atomic weights assigned to the rare-earth elements turned out to be incorrect later on. These wrong values of the atomic weights can be explained by the fact that Mendeleev assumed that the most common valency of the rare-earth elements was 2 and not 3 (*vide infra*).

If Mendeleev was to convince the chemical community of the fundamental character of his system, he had to explain his line of thoughts in more detail. Indeed, his pamphlet did not contain any evidence that might persuade other chemists of the validity of his assertions (Brooks, 2002). Over the course of the next two years (1869–1871), Mendeleev

labored at the clarification, illustration, refinement, and optimization of his periodic classification of the elements. Not surprisingly, the accommodation of the rare-earth elements formed an important part of Mendeleev's research program. During the second half of February 1869, Mendeleev drafted his initial article announcing the discovery of the periodic law and proposing the *Attempted System* as a useful classification of the elements. His paper "On the Correlation between the Properties of the Elements and Their Atomic Weights" was subsequently read by Nikolai Menshutkin on March 6, 1869, at the meeting of the newly founded Russian Chemical Society. Finally, after having received the proofs of the article on April 5, 1869, Mendeleev published his paper in the first volume of the society's new journal, the *Zhurnal Russkogo Khimicheskogo Obshchestva*, in the month of May of that year (Mendeleev, 1869b). This paper was also abstracted in the German language (Mendelejeff, 1869a,b). It should be mentioned that English translations of the most important papers on the periodic law, written by Mendeleev, can be found in the book of Jensen (2002).

As soon as he had finished the writing process, Mendeleev moved over to some experimental research, in the late spring or early summer of 1869. After all, there still remained a number of serious problems connected with his *Attempted System* at the beginning of 1869. Some elements, such as uranium, lead, and thallium, were wrongly accommodated in the system, due to their imprecisely determined atomic weights and doubtful valencies. Thus the atomic weight of uranium was too low, while thallium and lead had been given an incorrect maximum valency of 1 and 2 respectively. Other elements, such as tellurium and iodine, violated the atomic weight sequence as a consequence of their inversed placement which was necessary for the correct grouping of these elements. Mendeleev had also left a number of open places in his system and he boldly proclaimed that these represented some as yet undiscovered elements. Unfortunately, the first version of the periodic table did not prove very useful in determining the characteristic properties of unknown elements. It must be noted that Mendeleev's first representation of the periodic system did not exactly represent all the various chemical and physical relationships between the different elements. The most severe problem however found its origin in the seven elements (Er, Yt, In, Ce, La, Di, and Th) which remained outside the system (*vide supra*). Finally, Mendeleev had not been very clear in his article about the kind of chemical and physical properties of the elements that could be used in order to exemplify the principle of periodicity.

Mendeleev thus began by investigating the atomic volumes of the elements as a possible periodic function of the atomic weight, hoping that his research would confirm the periodic law. His research on the atomic volumes of the elements illustrated that this physical property tended to rise in each short period, reaching a maximum value in the halogens and alkali

metals. But when Mendeleev started examining the longer periods of his system, he first noticed a decrease in the atomic volumes, reaching a minimum at the end of the first half of the period (around the transition metal triads). Once arrived in the second part of the period, the atomic volumes started to increase again. In the case of uranium however, Mendeleev noted a decrease instead of the expected increase. Mendeleev took this as a sign that uranium had been incorrectly accommodated in the *Attempted System*, and he removed the element from its original position in the table between cadmium and tin during the summer of 1869. Mendeleev must have realized that an alteration of the atomic weight and valency of uranium were needed in order to change its position in the system. During the month of August 1869, Mendeleev started writing a paper about his experimental results *Concerning the Atomic Volumes of Simple Bodies* (Gordin, 2004). In August 1869, Mendeleev attended the Second Congress of Russian Physicians and Naturalists in Moscow where he delivered a lecture about his work on the atomic volumes, emphasizing that a comparison of specific weights and specific volumes of the elements belonging to different rows showed to some extent the naturalness of his periodic system.

The naturalness of the system had indeed been proven on the basis of a physical property of the elements, but Mendeleev decided to check whether the chemical properties of the elements would exhibit a periodic relation as well. He immediately turned to an investigation of the higher salt-forming oxides and presented his results on October 2, 1869, during a meeting of the Russian Chemical Society in a paper entitled "On the Quantity of Oxygen in Metal Oxides and on the Valency of the Elements" (Mendeleev, 1870). Mendeleev explained that the periodicity in the valency would only manifest itself in the higher oxides. Mendeleev distinguished seven limiting forms of salt-forming oxides, depending on the highest known oxidation number of a given element: R_2O , R_2O_2 (= RO), R_2O_3 , R_2O_4 (= RO_2), R_2O_5 , R_2O_6 (= RO_3), and R_2O_7 . Every element that is able to react with oxygen forms an oxide, the composition of which can be represented by one of these seven formulae. Mendeleev moreover emphasized the need of considering the salt-forming oxides, since chemists could be drawn to erroneous conclusions about the valency of the elements by mistaking peroxides for oxides (*vide infra*). During the winter of 1869, Mendeleev measured the heat capacity of uranium metal, since this would enable him to correct the atomic weight of uranium (old symbol: Ur). He consequently changed the value from 116 to 240 in early 1870.

Due to the recent discoveries of the rare-earth elements, most of their chemical and physical properties were not yet known in 1869, and Mendeleev had to manage with the limited information that was available at that time. As a consequence, Mendeleev did not succeed in correctly accommodating these elements when he constructed his *Attempted System*. This is not surprising given the fact that Mendeleev still adhered

to the old Berzelian atomic weights of the rare-earth elements. None of these values corresponded with the modern atomic weights. From the well known relationship between the atomic weight (AW) of an element (X), its equivalent weight (EW), and its valency (V):

$$AW(X) = EW(X) \times V(X), \quad (1)$$

one can conclude that these atomic weights were incorrectly determined due to an erroneous estimation of the valence of these elements. Thus, if Mendeleev was using the wrong valency number for some element X , say V_1 , this logically implied a miscalculation of the atomic weight AW_1 :

$$AW_1(X) = EW_1(X) \times V_1(X), \quad (2)$$

where use was made of Eq. (1). In order to obtain the correct atomic weight AW_2 , a correction of the valency number, from V_1 to V_2 , is necessary:

$$AW_2(X) = EW_2(X) \times V_2(X). \quad (3)$$

Due to the constancy of the equivalent weight:

$$EW_1(X) = EW_2(X), \quad (4)$$

eqs. (2) and (3) can be rewritten as follows:

$$\frac{AW_1(X)}{V_1(X)} = \frac{AW_2(X)}{V_2(X)}. \quad (5)$$

Otherwise stated, there exists a relationship between Mendeleev's atomic weight values (AW_1) and the corresponding modern values (AW_2):

$$AW_1(X) = AW_2(X) \times \frac{V_1(X)}{V_2(X)}, \quad (6)$$

which makes it possible to determine the valency as used by Mendeleev in 1869 (V_1):

$$V_1(X) = \frac{AW_1(X)}{AW_2(X)} \times V_2(X). \quad (7)$$

For example, lanthanum was allotted an atomic weight of 94 (AW_1) in Mendeleev's *Attempted System*. The modern value for lanthanum's atomic weight is 138.9 (AW_2) and as all the rare-earth elements typically exhibit the +III oxidation state, its modern valency is 3 (V_2). With the aid of Eq. (7), the valency number V_1 as used by Mendeleev in the beginning of 1869 can be established:

$$V_1(\text{La}) = \frac{AW_1(\text{La})}{AW_2(\text{La})} \times V_2(\text{La}) = \frac{94}{138.8} \times 3 = 2.03 \approx 2. \quad (8)$$

Apparently, Mendeleev believed the valency of lanthanum to be 2 instead of 3. As a consequence, he used the incorrect atomic weight of 94. Application of Eq. (7) to the other six elements with wrong atomic weight values, leads to the following valencies used by Mendeleev:

$$V_1(\text{Er}) = \frac{AW_1(\text{Er})}{AW_2(\text{Er})} \times V_2(\text{Er}) = \frac{56}{167.2} \times 3 = 1.004 \approx 1, \quad (9)$$

$$V_1(\text{Y}) = \frac{AW_1(\text{Y})}{AW_2(\text{Y})} \times V_2(\text{Y}) = \frac{60}{88.9} \times 3 = 2.02 \approx 2, \quad (10)$$

$$V_1(\text{Ce}) = \frac{AW_1(\text{Ce})}{AW_2(\text{Ce})} \times V_2(\text{Ce}) = \frac{92}{140.1} \times 3 = 1.97 \approx 2, \quad (11)$$

$$V_1(\text{Di}) = \frac{AW_1(\text{Di})}{AW_2(\text{Di})} \times V_2(\text{Di}) = \frac{95}{142} \times 3 = 2.007 \approx 2, \quad (12)$$

$$V_1(\text{In}) = \frac{AW_1(\text{In})}{AW_2(\text{In})} \times V_2(\text{In}) = \frac{75.6}{114.8} \times 3 = 1.98 \approx 2, \quad (13)$$

$$V_1(\text{Th}) = \frac{AW_1(\text{Th})}{AW_2(\text{Th})} \times V_2(\text{Th}) = \frac{118}{232} \times 3 = 2.03 \approx 2. \quad (14)$$

It follows from Eqs. (8)–(12) that the known rare-earth elements were considered to be divalent instead of trivalent. Their oxides were generally represented by the formula RO and the higher oxide of cerium was denoted by the formula R₂O₃. Therefore, all atomic weights were incorrectly determined, and this explains why Mendeleev was not able to accommodate these elements into his periodic system. Only with the correct atomic weights at hand, could one try to accommodate them. But this also necessitated a change in valency from 2 to 3. Although Mendeleev would be the first in proposing this modification of valency number, he only did so at the end of the first half of 1870. Before that, during the period 1869–1870, Mendeleev continued to look upon the rare-earth elements as being divalent and he used the wrong atomic weights throughout. On the other hand, it should be noted that Mendeleev started to doubt the positions of the rare-earth elements from the very outset. As he admitted in his 1869 article *On the Correlation between the Properties of the Elements and Their Atomic Weights* (Mendeleev, 1869c; Mendelejeff, 1869c): “With respect to the position of some elements, there exists, quite understandably, complete uncertainty. In particular, this holds for those elements that are little studied and whose correct atomic weight

has hardly been established with any certainty. Among these are, for example, yttrium, thorium, and indium.”

3.2 Rare Earths as a Primary Group

When Lavoisier defined a chemical element in 1789, 26 elements were actually known. Eighty years later, in 1869, a total of 36 new chemical elements had been discovered. As a consequence, more and more chemists felt the need for a systematic organization. Instead of building a periodic table, as Mendeleev did in 1869, they quickly inclined towards putting together elements with similar physical and chemical characteristics, ending up with a network of small, so-called *natural groups*. Examples of natural groups are the highly reactive halogens (F, Cl, Br, I) and the silvery colored and water-reactive alkali metals (Li, Na, K, Rb, Cs). The interesting fact is that Mendeleev clearly recognized the similarity in chemical and physical properties of the rare-earth elements. He therefore considered them as the members of a natural group and he proclaimed this point of view in his 1869 article (Mendeleev, 1869c; Mendelejeff, 1869c): “Only with regard to some groups of elements are there no doubts that they form a whole and represent a natural order of similar manifestations of matter. . . . Such groups are: the halogens, the alkaline earth metals, the nitrogen group, and also—in part—the sulfur group, the companions of platinum, the companions of cerium, and a few others.” Note that Mendeleev considered the other rare earths as the companions of cerium. As a consequence, and in complete analogy with the alkali metals and the halogens, Mendeleev tried to accommodate the rare earths in the periodic table as a group. This fact is clearly exemplified in the *Attempted System* where all the rare-earth elements (Er, Yt, Ce, La, and Di) were grouped together at the bottom of the system. However, Mendeleev understood that the rare earths constituted a very special group of elements and that the whole accommodation issue had its root in the puzzling nature of this elemental group. According to Mendeleev (1869c), “the most interesting problem was the arrangement of elements having such similarities as cerium.”

In order to understand why Mendeleev discriminated this group from the other natural groups (alkali metals, halogens, etc.), it will be necessary to go into a detailed consideration of the construction methodology of the periodic table. In short, a two-step process is needed in order to build a periodic table from scratch. First, all the elements have to be ordered according to increasing atomic weight. Notice that in the modern periodic tables, the ordering is according to increasing atomic number (i.e., the number of protons in the nucleus). This *primary classification* results in a long horizontal sequence of elements, and has been called the *Mendeleev Line* by Henry Bent (Bent, 2006). It will be noted that certain chemical and

physical properties of the elements recur periodically. Therefore, the second step, termed the *secondary classification*, consists of partitioning this Mendeleev Line at certain well defined loci and placing the different sections (i.e., periods) underneath each other so that the elements with similar properties will fall into the same vertical column, thus forming the natural groups and representing the periodic law graphically.

One can conclude at this point that natural, elemental groups (e.g., Li, Na, K, ..., Ag) are formed during the secondary classification. Within such a vertical group, the atomic weights of the congeners will vary in a stepwise way. Thus in the case of the group {Li, Na, K, ..., Ag}, one notices the following sequence of "jumps" between the atomic weights: $7 \rightarrow 23 \rightarrow 39 \rightarrow \dots \rightarrow 108$. One could denominate such a natural group of elements by the term *secondary group*. The members of such a secondary group will be nominated *secondary elements*. Hence, a secondary group can be defined and recognized as follows: (1) Secondary groups are always formed during the secondary classification of the elements; (2) There exists a stepwise relationship between the atomic weights of the congeners. Some examples of secondary groups are the alkali metals, the halogens, the alkaline earth metals, and the noble gases.

In sharp contrast with this type of natural groups, some other groups, e.g., the cerium group {Ce, La, Di}, are formed at an earlier stage of the construction methodology, namely during the primary classification. Worded somewhat differently, due to the fact that the elements constituting such groups succeed one another sequentially in the Mendeleev Line (e.g., Ce = 92, La = 94, Di = 95), the formation of these groups will be noticed during the primary classification. Within such a horizontal group, the atomic weight of the congeners will remain almost constant. Thus in the case of the elemental group {Ce, La, Di}, one observes the following sequence of atomic weights: $92 \rightarrow 94 \rightarrow 95$. Such a natural group of elements can be denominated by the term *primary group* and their congeners by the name *primary elements*. Hence, primary groups can be defined and recognized as follows: (1) Primary groups are always formed during the primary classification of the elements; (2) There exists a steady, almost constant relationship between the atomic weights of the congeners. Other examples of such primary groups are the iron group {Fe = 56, Ni = 59, Co = 59}, the platinum group {Pt = 197.1, Ir = 198, Os = 199}, the palladium group {Rh = 104.4, Rn = 104.4, Pl = 106.6} (in Mendeleev's nomenclature, Rn represented ruthenium and Pl represented palladium), and the erbium group {Er = 56, Yt = 60}. Since the rare-earth elements constituted two primary groups, {Ce, La, Di} and {Er, Yt}, Mendeleev (1869c) considered these groups to be special, because their congeners exhibited atomic weight values which were very close to each other, a fact not to be observed in the "normal" case of secondary groups where the congeners have radically different atomic weights.

At least four important consequences can be drawn from the existence of primary groups. First of all, Mendeleev naturally wondered how one should depict both primary and secondary groups within his *Attempted System*. In contrast to the modern periodic tables, the secondary groups were lying horizontally, whereas the primary groups were depicted vertically. A more significant consequence of the existence of primary groups within the periodic system is their so-called *transitional function*. Mendeleev got this idea when he was examining his *Attempted System*. It appeared to him that the elements of the primary groups at the upper part of his system represented some sort of transition between two (sub)- periods in the periodic table. He remarked that the upper members of the fourth column (Mn, Fe, Co, Ni, Zn) formed a transition to the lower members of the (third) column in which Ca, K, Cl, and similar elements were found, so that the properties and atomic weights of cobalt and nickel, chromium, manganese, and iron represented a transition from copper and zinc to calcium and potassium. At the beginning of 1869, Mendeleev's views on the matter were still rather intuitive and somewhat vague. Indeed, it was not easy to perceive the transitional function of the iron group, the palladium group, and the platinum group in the *Attempted System*. As a consequence of fixing all his attention on the *Attempted System*, Mendeleev immediately recognized how the two primary groups, {Ce, La, Di} and {Er, Yt}, at the bottom part of his system, helped in connecting the periods of the main core. It thus seemed that these primary groups were furnished with a transitional function as well. This brings us to the third important consequence of the existence of primary groups in Mendeleev's classification of the chemical elements. Due to the fact that both the transition metal groups (iron, palladium, and platinum group) and the rare-earth groups (cerium and erbium group) exhibited a transitional function, Mendeleev emphasized the similarity between these two sets of groups. Nevertheless, Mendeleev finally decided not to include the transition metal groups in the lower rows with the two rare-earth groups due to a difference in the basic/acidic properties of the oxides between the congeners of these two sets of groups. The rare earth – transition metal analogy was further exemplified by Mendeleev in his article "Concerning the Atomic Volumes of Simple Bodies" (Mendeleev, 1871; Mendelejeff, 1870). Mendeleev also emphasized the similarity in magnetic properties between the elements of the cerium group and those of the iron group. Repeated references to the rare earth – transition metal analogy were also made in his article "On the Quantity of Oxygen in Metal Oxides and on the Valency of the Elements" (Mendeleev, 1870). A fourth and last consequence of the existence of primary groups is their problematic nature, undermining both the periodic law and the characterization of elements as being defined by their atomic weight. Mendeleev noticed that when the elements are arranged according to their atomic weights, the elements display a distinct periodicity in their

properties. This is clearly seen in the series Li, Be, B, C, N, O, and F, where Li and F are monovalent, Be and O are divalent, B and N trivalent and C tetravalent. The same behavior is found for the series Na, Mg, Al, Si, P, S, and Cl. However, in the case of primary groups, there were of course regular and gradual changes in the size of atomic weights, but these were not accompanied by regular and gradual changes in the distinctive properties of the elements. In the case of the cerium group {Ce, La, Di}, for example, there was a small gradual increase in atomic weight, but the valency remained constant. The same could be said for the iron group, palladium group, platinum group, and the erbium group. The generality of the periodic law got undermined due to the presence of primary groups in the periodic system. This was one of the core problems of the rare-earth elements, laying at the basis of their problematic accommodation.

Mendeleev recognized the dual sense of the nature of chemical elements. He clearly distinguished between the elements as *simple substances* and the elements as *basic substances*. *Simple substances* can be characterized by the plethora of secondary properties (color, taste, smell, etc.), and are therefore observable and isolable (Paneth, 2003). *Basic substances* on the other hand are completely unobservable to our senses. This does not imply however that they are completely devoid of properties. Mendeleev was of the opinion that the more abstract, basic substances were characterized by their atomic weight, and he therefore used this property in accommodating all the chemical elements in his system. According to Mendeleev, the atomic weight of an element determined its place in the periodic table. He concluded for this reason that the magnitude of the atomic weight determined the character of an element to the same extent that the molecular weight determines the properties and many of the reactions of a compound substance. An important consequence of taking the atomic weight as the characteristic property of basic substances was the possibility of distinguishing between the (chemically and physically very similar) congeners of a certain elemental group in the periodic table. The natural group of alkali metals, {Li = 7, Na = 23, K = 39, Rb = 85.4, Cs = 133}, for example, consisted of five metals which shared a lot of similar properties: metallic luster, low melting points and densities, a pronounced reactivity with respect to water, a strongly oxidizing character, etc. It thus seemed that the differences in atomic weights were the only possible way to differentiate between these analogous elements. "Similar elements [in chemical and physical properties] possess different atomic weights," Mendeleev proclaimed (Mendeleev, 1869b). But in the case of the cerium group {Ce = 92, La = 94, Di = 95}, the difference in atomic weights was scarcely noticeable. Indeed, one recalls that in sharp contrast with the secondary groups, which were characterized by a stepwise relationship between the atomic weights of the secondary elements, primary groups represented a steady and almost constant relationship between the atomic weights of the primary elements. Mendeleev

noticed that this observation was not limited to the members of the cerium group. It turned out that similar apperceptions could be made with regard to the transition metal groups, for instance nickel and cobalt, whose atomic weights are very close to each other. Rhodium, ruthenium, and palladium on the one hand, iridium, osmium, and platinum on the other are also elements which closely resemble one another, and which have similar atomic weights. Iron and manganese have similar properties and their atomic weights are also very similar. This implied that, in the case of primary groups, no differentiation between the congeners was possible anymore on the basis of their atomic weights. Otherwise stated, while secondary elements could still be characterized by their atomic weights, primary elements, on the other hand, could not be characterized anymore by the atomic weight. The question naturally presents itself as to how one should differentiate between primary elements. According to Mendeleev, these elements were characterized by “internal differences of matter” (Trifonov, 1970).

Here ended the first period of Mendeleev’s research on the periodic law which lasted from 1869 till the end of the first half of 1870. Mendeleev’s viewpoints could be summarized as follows. According to his opinion, chemists had to draw a sharp distinction between primary (i.e., rare earths, transition metals) and secondary elements (i.e., alkali metals, halogens). Such a differentiation should also be made on the level of primary and secondary groups. The essence of the difficult accommodation of the rare earths in the periodic table rested on the fact that these elements constituted a primary group. Their problematic nature raised a number of serious problems. Both the principle of periodicity and the characterization of primary elements on the basis of their atomic weights became undermined. Mendeleev was also tempted in drawing an analogy between the rare-earth elements and the transition metals on the basis of their transitional functions in the periodic system, and he started questioning the simplicity of these elements on a closer study of the primary groups. He nevertheless continued to use the old atomic weights and erroneous valencies for the rare-earth elements, and his unremitting adherence to the *Attempted System* moreover troubled his views with regard to the different relationships between the chemical and physical properties of these elements.

3.3 Mendeleev’s Natural System of Elements

Mendeleev had been working on the optimization of the periodic law for quite some time now. He had always preferred the long form table (i.e., his *Attempted System*), but in November 1870, Mendeleev created a short form table, his *Natural System of the Elements* (Figure 5) (Mendeleev, 1871; Mendelejeff, 1870). In a long form of the periodic table, the d-block elements are separated from the main group elements, whereas this is

T a b e l l e II.

Reihen	Gruppe I.	Gruppe II.	Gruppe III.	Gruppe IV.	Gruppe V.	Gruppe VI.	Gruppe VII.	Gruppe VIII.
	R ⁰	RO	R ⁰	RR ⁰ RO ⁰	RR ⁰ R ⁰	RR ⁰ RO ⁰	RR ⁰ R ⁰	RO ⁰
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Cr=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Su=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Hf=138	?Co=140	—	—	—	—
9	(—)	—	—	—	—	—	—	—
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	—
12	—	—	—	Th=231	—	U=240	—	—

FIGURE 5 Mendeleev's Natural System of the Elements (1871). Reproduced from Mendelejeff (1871).

not the case in a short form of the periodic table. Mendeleev's *Natural System of the Elements* remained the standard format during the next decades, and it succeeded in exhibiting a number of new relationships between the chemical elements (e.g., the close connection between s-, p-, d-, and f-block elements among other aspects).

In following the above mentioned construction methodology (Section 3.2), partitioning the Mendeleev Line after each halogen element, Mendeleev quickly obtained a first sequence of seven elements (Li, Be, B, C, N, O, F) which he denoted as "a short period or series." The lightest element, hydrogen, was solitarily situated above this period, and Mendeleev therefore decided to name it the first series. As a consequence, (Li, Be, B, C, N, O, F) belonged to the second series, (Na, Mg, Al, . . .) to the third, etc. However, during the secondary classification, both short and long periods were obtained. Mendeleev noticed that not all of the presently known elements could be placed in short series. Thus, after the third short periods of seven elements, a fourth and longer period (17 elements long) was obtained (Figure 6).

Because of these longer periods, not all of the main block elements were grouped together (e.g., F and Cl were separated from Br and I). Mendeleev therefore had to pursue the secondary classification and the longer periods were cut in half. By partitioning the Mendeleev line before Cu, Ag, and Au, Mendeleev obtained a modified periodic table of chemical elements (Figure 7).

As a result, the fourth period gave rise to two series (the fourth and the fifth) of 10 and 7 elements respectively. The fourth series was termed an *even series*, while the fifth series was called an *odd series*. Mendeleev

H																	
Li	Be	B	C	N	O	F											
Na	Mg	Al	Si	P	S	Cl											
K	Ca	–	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	–	–	As	Se	Br	
Rb	Sr	–	Zr	Nb	Mo	–	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	
Cs	Ba	–	Ce	–	–	–	–	–	–	–	–	–	–	–	–	–	–
–	–	–	–	Ta	W	–	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	–	–	
–	–	–	Th	–	U	–	–	–	–	–	–	–	–	–	–	–	

FIGURE 6 Mendeleev's table with eight periods.

1	H																
2	Li	Be	B	C	N	O	F										
3	Na	Mg	Al	Si	P	S	Cl										
4	K	Ca	–	Ti	V	Cr	Mn	Fe	Co	Ni							
5	Cu	Zn	–	–	As	Se	Br										
6	Rb	Sr	–	Zr	Nb	Mo	–	Ru	Rh	Pd							
7	Ag	Cd	In	Sn	Sb	Te	I										
8	Cs	Ba	–	Ce	–	–	–	–	–	–							
9	–	–	–	–	–	–	–										
10	–	–	–	–	Ta	W	–	Os	Ir	Pt							
11	Au	Hg	Tl	Pb	Bi	–	–										
12	–	–	–	Th	–	U	–	–	–	–							

FIGURE 7 Mendeleev's table with 12 periods.

furthermore observed that there exists a very marked difference between the corresponding members of the odd and even series (with the exception of the first two), while, among themselves, the members of the odd series, as well as the members of the even series display much greater analogies. For example, the members of the fourth and sixth series show more similarities among themselves than they do with the members of the fifth or seventh series. Indeed, the alkali metals K and Rb (situated in the fourth and sixth series) are distinctly different from the coinage metals Cu and Ag (situated in the fifth and seventh series). Similarly, chlorine, bromine, and iodine (positioned in the third, fifth, and seventh series, respectively) are all halogens, while Mn (located in the fourth series) certainly is not. In a certain sense, Mendeleev was alluding to the difference in properties between the main block elements (i.e., s-block and p-block elements) and the d-block elements. This was emphasized in his *Natural System* by alternating the elements to the left and the right of each column. At the same time Mendeleev arranged all of the elements which could not be placed in the short periods in order of their properties and atomic weights between the last member of the even series and the first member of the odd series. In this manner Fe, Co, and Ni formed a transition from Cr and Mn, on the one side, to Cu and Zn, on the other.

Mendeleev was thus aided significantly by his construction of the short form table in defining the transition metals more clearly than before as those elements which connected the even and the odd series. Two other triads of transition metals could moreover be discerned in the *Natural System of Elements*. Just as Fe, Co, and Ni follow the 4th series, so Ru, Rh, and Pd follow the 6th, and Os, Ir, and Pt the 10th. Each large period of 17 members thus consisted of two series (one even and one odd), along with the intermediate series of elements given above. Since the intermediate members did not correspond to any of the seven groups of the short periods, they formed an independent group (the eighth, which was indicated by the Roman numeral VIII). Mendeleev also emphasized that the members of this group resembled one another to the same extent as the corresponding members of the even series, with the only difference that they constituted three primary groups, instead of secondary groups as in the case of the elements from the groups I–VII.

Due to the table layout of Mendeleev's *Natural System of the Elements*, consisting of eight groups (I–VIII) and 12 series (1–12), each element (X) could be characterized by two coordinates: its group number (G) and its series number (S). Sodium for example, was located in the first group and the third series, and was therefore given the element coordinates I-3. Magnesium was located in the place II-3, and titanium was characterized by the element coordinates IV-4. The improved format of Mendeleev's table had revealed a number of interesting relationships between the properties of the elements. Encouraged by this new information, Mendeleev began to focus all his attention on predicting the properties of the as yet undiscovered elements (i.e., *eka-boron* in III-4, *eka-aluminium* in III-5, and *eka-silicon* in IV-5).

The *Natural System of Elements* (Figure 5) also contained corrected atomic weights. In his paper "On the Placement of Cerium in the Periodic System of Elements" (Mendelejew, 1870), Mendeleev admitted that the atomic weights of indium, uranium and cerium (and probably its companions, the other rare-earth elements) should be modified because these elements did not fit in the periodic table on the basis of either the formulae of their oxides or their properties according to the periodicity (Trifonov, 1970). He realized that a change in valency would be necessary in order to correct the atomic weight values of the rare earths. The usual representation of their oxides by the formula RO had thus to be modified. Mendeleev was the first in assuming the rare earths to be trivalent, instead of divalent, and he therefore proposed the general formula R_2O_3 for the rare-earth oxides. In the case of cerium, which has two oxidation states, Mendeleev proposed to assign the formula Ce_2O_3 to the oxide of cerium in the lower oxidation state and CeO_2 to the higher oxide (Trifonov, 1966). Similar statements were repeated in his article "Concerning the Natural System of the Elements and Its Application in Determining the Properties

of Undiscovered Elements'' (Mendeleev, 1871; Mendelejeff, 1870). These valency shifts also implied that the atomic weights used in his 1869 periodic table would have to be increased by a factor of 1.5:

$$AW_1(X) = AW_2(X) \times \frac{V_1(X)}{V_2(X)} = AW_2(X) \times \frac{3}{2}, \quad (15)$$

where use was made of Eq. (6). AW_1 and V_1 were taken to represent the new atomic weight values and valency numbers, respectively, while AW_2 and V_2 were used for the old values. Application of Eq. (15) to the set of seven elements with incorrect atomic weights leads to the following atomic weight values:

$$AW_1(\text{Er}) = AW_2(\text{Er}) \times \frac{V_1(\text{Er})}{V_2(\text{Er})} = 56 \times \frac{3}{1} = 168 \quad [178], \quad (16)$$

$$AW_1(\text{Y}) = AW_2(\text{Y}) \times \frac{V_1(\text{Y})}{V_2(\text{Y})} = 60 \times \frac{3}{2} = 90 \quad [92], \quad (17)$$

$$AW_1(\text{In}) = AW_2(\text{In}) \times \frac{V_1(\text{In})}{V_2(\text{In})} = 75.6 \times \frac{3}{2} = 113.4 \quad [113], \quad (18)$$

$$AW_1(\text{Ce}) = AW_2(\text{Ce}) \times \frac{V_1(\text{Ce})}{V_2(\text{Ce})} = 92 \times \frac{3}{2} = 138 \quad [138], \quad (19)$$

$$AW_1(\text{La}) = AW_2(\text{La}) \times \frac{V_1(\text{La})}{V_2(\text{La})} = 94 \times \frac{3}{2} = 141 \quad [140], \quad (20)$$

$$AW_1(\text{Di}) = AW_2(\text{Di}) \times \frac{V_1(\text{Di})}{V_2(\text{Di})} = 95 \times \frac{3}{2} = 142.5 \quad [140], \quad (21)$$

$$AW_1(\text{Th}) = AW_2(\text{Th}) \times \frac{V_1(\text{Th})}{V_2(\text{Th})} = 118 \times \frac{4}{2} = 236 \quad [231]. \quad (22)$$

The values in square brackets are those that were effectively used by Mendeleev in 1870. Notice that the atomic weight of erbium was tripled, while the atomic weight of thorium was doubled, just as in the case of uranium:

$$AW_1(\text{U}) = AW_2(\text{U}) \times \frac{V_1(\text{U})}{V_2(\text{U})} = 116 \times \frac{6}{3} = 232 \quad [240]. \quad (23)$$

After having changed the atomic weights of indium, uranium, and cerium, Mendeleev decided to check the correctness of the new values by determining the heat capacity of these elements (Trifonov, 1970).

3.4 Homologous Accommodation Methodology

When the atomic weight of an element X is changed, this logically implies a change in the position of X within the periodic table of elements. Thus, due to the atomic weight corrections of indium, uranium, cerium, lanthanum, didymium, yttrium, erbium, and thorium, all eight elements had to be removed from their usual place, and they had to be accommodated differently. As a consequence, Mendeleev switched from placing the rare-earth elements as a group in the periodic system to the individual placement of each element separately. The change in the atomic weight of indium (from 75.6 to 113) alluded to the fact that it might be accommodated in the position III-5, between cadmium (112) and tin (118). This position had formerly been occupied by uranium. Further support for the relocation of indium was provided by its atomic volume (15.5) which lay midway between the atomic volumes of cadmium (13.0) and tin (16.4). The accommodation of cerium went smoothly as Mendeleev had correctly determined its atomic weight and oxide formulae. Recall that cerium can exhibit two oxidation states (+III and +IV), making its placement in the fourth group very natural. On the basis of its higher degree of oxidation Mendeleev decided to place cerium in the titanium group, in place IV-6 (Figure 5). The placement of lanthanum, didymium and the other rare earths proved much more difficult. Mendeleev finally decided to locate yttrium in position III-4. Lanthanum seemed to fit in position III-6 and didymium was finally given the element coordinates V-6, although Mendeleev was still hesitating and playing with the idea of placing it with lanthanum in the position III-6. All rare-earth elements were thus placed as homologues of the other elements throughout the periods of the periodic system in the groups I–VIII according to a *homologous accommodation methodology*. We will subsequently denote this type of accommodation the *Mendeleev Method*. It must be noted however, that while the individual accommodation of the rare-earth elements had been an interesting step forward, this did not remove all problems. Mendeleev had always used “a web of analogies” in determining the positions of the chemical elements, but this methodology could no longer be applied in the case of the rare earths. The rare-earth elements exposed a serious weakness in Mendeleev’s approach to solving the placement of elements in his periodic system. Mendeleev therefore remained very doubtful as to the new positions of the rare-earth elements. Nevertheless, Mendeleev held onto his original conception of the periodic law and he would not permit himself to allow exceptions for the rare-earth elements or any other element (Brooks, 2002).

Mendeleev drew five important conclusions from these rare-earth accommodations. The first one concerned the oxidation states of the rare-earth elements. Lanthanum, a typically trivalent element, was placed

in the third group (III-6). Cerium which could be trivalent as well as tetravalent was accommodated in the fourth group (IV-6). Due to the fact that didymium was located in the fifth group (V-6), Mendeleev presumed that this element could be pentavalent. In other words, the validity of the homologous accommodation methodology could be proven by demonstrating the pentavalent character of didymium. A second consequence of the rare-earth accommodation was the fact that 17 positions remained vacant between the elements cerium ($Ce = 138$) and tantalum ($Ta = 182$). Mendeleev predicted the existence of 17, still undiscovered, rare-earth elements on the basis of their being flanked by two rare earths, cerium, with an atomic weight of 138, and erbium, with an atomic weight of 178. Thirdly, Mendeleev intuitively recognized the existence of the *lanthanide contraction*, because of the close similarities in properties of the element pairs (molybdenum, tungsten), (niobium, tantalum), (antimony, bismuth), and (tin, lead). Fourthly, Mendeleev felt embarrassed by the fact that the seventh period was completely empty, and he put forward the hypothesis that the absence of an entire row of elements is due to their limited stability. Finally, Mendeleev also withdrew his previous claims about the analogy between the rare earths and the iron group. For instance, he observed that the elements of the cerium group are more difficult to reduce than those of the iron group. He also noticed that their normal oxides possess strongly basic properties and do not give characteristic compounds with ammonia and cyanide, in contrast to the iron group elements.

3.5 Mendeleev's Rare-Earth Research

Mendeleev finished writing his paper "Concerning the Natural System of the Elements and Its Application in Determining the Properties of Undiscovered Elements" on November 29, 1870 and he presented his work during a meeting of the Russian Chemical Society in early December 1870 (Mendeleev, 1871). With the predicted properties at hand, Mendeleev soon tried to find the unknown elements. The position of eka-silicon (IV-3) implied that its properties would lie midway between those of titanium and zirconium, and Mendeleev therefore thought it best to initiate his search for this element in the minerals of titanium and zirconium. Two days after the meeting of the Russian Chemical Society, on December 5, 1870, Mendeleev sent a petition to the rector of the University of St. Petersburg, K. F. Kessler, requesting him to contact the Mining Institute to ask them for samples of rare minerals he needed for his scientific work. Mendeleev stressed how especially important it was for him to obtain as large an amount of titanium minerals as possible, and specifically rutile (TiO_2), ilmenite ($FeTiO_3$), and also other minerals: zircon, orthite, or cerite and eschynite. The reason why Mendeleev asked for some specimens of rutile, ilmenite and zirconium is clear. But his

requests of orthite, cerite, and eschynite are less evident. Both cerite and eschynite are rich in cerium (and to a lesser degree also in lanthanum and yttrium). The mineral orthite, on the other hand, is not only abundant in cerium, it also contains substantial amounts of the other rare-earth elements. Obviously, Mendeleev was not only planning to discover the unknown eka-silicon, he also hoped to perform some experimental research on the rare earths in order to resolve their problematic accommodation, and to prove the validity of his homologous accommodation methodology.

Around the same time in July 1871, Mendeleev also started composing his German landmark article on the periodic law. It was translated into German by Felix Wreden and appeared in *Liebig's Annalen* in November 1871, symbolizing Mendeleev's last research paper on the periodic law (Mendelejeff, 1871). According to Brooks (2002), Mendeleev spent considerable time trying to separate the four known rare-earth elements over the course of about one year, but he only met with failure. The difficulty was compounded because two of these rare earths (didymium and erbium) later turned out to be mixtures of several elements. On December 20, 1871, Mendeleev decided to abandon all research on the rare-earth metals, and he set off on a gas project in search of the luminiferous ether (Gordin, 2004). Later he still published papers on the applications of the periodic law to the rare earths (Mendeleev, 1873; Mendelejeff, 1873a,b), on the corrected atomic weight of yttrium (Mendeleev, 1872), and on scandium (Mendeleev, 1881; Mendelejeff, 1881).

This was the end of Mendeleev's experimental research on the periodic law as well as his rare-earth investigations. Without a doubt, Mendeleev had grasped the essence of the difficult accommodation of the rare earths better than anyone else. His train of thought had been meticulously written down in a number of papers on the periodic law during the period 1869–1871. Mendeleev's landmark paper of 1871 in particular proved most valuable for the next generation of chemists who were on the verge of starting their own rare-earth studies (Section 4). But Mendeleev had not only circumscribed the rare-earth problem, he had also significantly aided in partly resolving the problem of their accommodation. Thus Mendeleev had corrected the atomic weight values of the rare-earth elements by increasing their valency from 2 to 3, and he had attempted to accommodate these metals on an individual basis according to a homologous placement. Yet, a definite proof as to the validity of this accommodation methodology was still lacking.

It can be mentioned here that another pioneer of the periodic system, the German Julius Lothar Meyer (1830–1895) did not list the rare earths in his first periodic table, because he was not convinced that the rare earths were genuine elements (van Spronsen, 1969). He also found that their atomic weights had not been determined with sufficient accuracy.

Later, he accepted the elemental nature of the rare earths and he tried to place them in the periodic table according to a homologous accommodation methodology, as Mendeleev did. In 1876, Meyer placed cerium, erbium, and yttrium in the boron group as trivalent elements, but he placed lanthanum in the column of the tetravalent elements.

4. BOHUSLAV BRAUNER AND SIR WILLIAM CROOKES

4.1 Brauner's Rare-Earth Research

The Czech chemist Bohuslav Brauner (1855–1935) (Figure 8) read Mendeleev's 1871 paper about six years later (Brauner, 1930; Druce, 1944). It made such an impression on him that he decided to refocus his experimental research on finding a solution for the question of the position of the rare earths in the periodic system. Brauner became the main defender of the periodic system in late nineteenth century. His rare-earth research has been of great importance in the further resolution of the so-called "rare-earth crisis," i.e., the problematic accommodation of the rare earths in the periodic system. It was especially Mendeleev's change of the atomic weights that had drawn Brauner's attention. It appears that although Brauner doubted the homogeneity (read: elementarity) of



FIGURE 8 Bohuslav Brauner (1855–1935). Photo and permission from Edgar Fahs Smith Collection.

erbium and terbium, he was quite sure that lanthanum, cerium, and didymium were genuine rare-earth elements. Brauner noticed that not only Mendeleev, but also Julius Lothar Meyer (1830–1895) had struggled with the accommodation of these elements in the periodic table. Whereas Mendeleev placed cerium in the fourth group (vertical), he was skeptical about the position of lanthanum and didymium. Meyer, on the other hand, placed cerium in the third group, lanthanum in the fourth group, and didymium provisionally in the sixth group. However, later on he placed all three elements in the third group. In a 1878 paper on the atomic weight of beryllium, Brauner gave his first personal view on the location of the individual members of the rare earths and he proposed to place the cerium metals in the eighth series (horizontal) of the periodic system as follows (Brauner, 1878):

III-8	IV-8	V-8
La = 139	Ce = 141.6	Di = 147

Brauner started his rare-earth research in 1878 when he was working in the laboratory of Robert Bunsen (1811–1899) in Heidelberg (Brauner, 1930). At that time he was working with Bunsen's calorimeter in order to determine the heat capacity of uranium metal. He wanted to prove that the atomic weight of uranium was 240, as predicted by Mendeleev with the aid of his periodic system. After having completed this research topic, he quickly turned to the problem of the accommodation of the rare earths in the periodic table. Brauner was initially trying to apply the above mentioned *Mendeleev Method*. His research program therefore consisted of three steps. First, Brauner would attempt to optimize the currently used fractionation methods in order to isolate the rare-earth elements and to determine the homogeneity of the obtained fractions. These investigations should help in deciding whether the rare-earth elements were really elementary, or rather mixtures of elements. Once this was settled, Brauner planned to establish the atomic weight values of the pure rare earths in order to arrange them according to their increasing atomic weight. With the correct sequence of rare earths at hand, all elements could be placed in the periodic table. Thirdly and most importantly, Brauner realized that he had to investigate the higher oxides of some rare earths, if he was to verify whether the valencies of these elements were in agreement with the number of the group to which they belonged. So, if lanthanum, cerium, and didymium would be genuine elements, and if their sequence as outlined above would prove correct, then Brauner was still to demonstrate the tetravalency of cerium and the pentavalency of didymium.

Therefore, Brauner was highly interested in the higher oxides of didymium. Mosander, de Marignac, Hermann, and Zschiesche had all observed that didymium forms besides the grey oxide Di_2O_3 a higher

oxide of a brown color, but they were unable to determine its true composition. Several other chemists, including Meyer, Cleve, Nilson, and Mendeleev had synthesized this higher oxide, but they had all ascribed it different formulae, ranging from DiO_2 to Di_4O_9 . Brauner on the other hand thought (and obviously hoped) that it would be Di_2O_5 , thus pointing to the pentavalency of didymium. If that brown oxide would really prove to be Di_2O_5 , this would also confirm didymium's accommodation in position V-8 in the periodic table and this would put didymium next to the elements N, P, V, As, Nb, Sb, (Di), Ta, and Bi, which also give two oxides R_2O_3 and R_2O_5 . With didymium (Di) placed at the position V-8, one would have the following horizontal series of oxides: Cs_2O , Ba_2O_2 (= BaO) La_2O_3 , Ce_2O_4 (= CeO_2), Di_2O_5 , ...

Establishing the pentavalency of didymium proved however much more difficult than expected. One of the main problems that Brauner had to cope with can be termed the "oxide problem." From the very outset of his research, Brauner made the crucial distinction between oxides and peroxides, noting that from the peroxides alone, there was not yet sufficient ground to conclude on the valency and placement of the elements in the system. Brauner was thus alluding to the fact that the peroxide anion, O_2^{2-} , contains two oxygen atoms with a valency of -1 , instead of -2 . An example can help to clarify this. If one considers hydrogen peroxide (H_2O_2) to be an oxide instead of a peroxide, then this would also imply that hydrogen has a valency of $+2$ instead of the correct valency number $+1$. Thus, by confusing the two types of oxygen compounds, mistaking peroxides for oxides, chemists could draw erroneous conclusions about the valency of the elements. Consequently, Brauner was led to the question of how to discern peroxides from oxides. Apparently, Mendeleev had already discussed the oxygen problem in his papers on oxygen compounds and peroxides, but Brauner was unaware of these publications. Mendeleev had tried to clarify this issue by showing that the theoretical distinction between peroxides and oxides could also be applied in a practical manner. He explained that all oxygen compounds could be divided into two groups. The first group consisted of the actual peroxides, which did not form salts, while the second group consisted of oxides yielding salts with the aid of mineral acids. In other words, it was the ability to form salts which, according to Mendeleev's opinion, should be taken as the criterion for the existence of higher oxides.

The search for a good method for the synthesis of Di_2O_5 was initiated in Heidelberg, in the laboratory of Bunsen in 1879. Brauner calculated that it had to be theoretically possible to obtain about 109.5 g of Di_2O_5 from 100 g of Di_2O_3 . Brauner only managed to get a maximum of 103.55 g of Di_2O_5 . During the remainder of his stay in Heidelberg (until 1880), Brauner made one fruitless attempt after the other, trying to obtain the pentoxide by another method. He tried to act on Di_2O_3 with oxygen, hydrogen peroxide, barium peroxide, but without success.

Brauner returned to Prague in 1880 and he obtained his degree of Doctor of Philosophy during the course of that same year. In the summer of 1880, Brauner succeeded to prepare a higher oxide of didymium by thermally decomposing didymium oxalate. He thus obtained 106.90 g of a brown oxide out of 100 g of Di_2O_3 , whose color remained unchanged during subsequent calcinations. Brauner had to ascertain whether it was an oxide or a peroxide. He thus immediately proceeded with his investigations and attempted to convert the pentoxide into the corresponding salts.

Meanwhile, Brauner was searching for a foreign inorganic laboratory where he could continue his rare-earth research. He decided in the autumn of 1880 to go to the laboratory of Sir Henry Enfield Roscoe (1833–1915) in Owens College in Manchester. Roscoe was particularly noted for his research on vanadium and for the photochemical investigations he performed in collaboration with Bunsen in Heidelberg in 1852, where he studied the formation of hydrogen chloride from hydrogen and chlorine. Five years later, Roscoe was called to the chair of chemistry at Owens College in Manchester. In view of the fact that Roscoe and Bunsen became lifelong friends, it seems very probable that Bunsen advised Brauner to head for Manchester. It was during his sojourn in Owens College that Brauner succeeded in demonstrating the tetravalent character of cerium for the very first time. He dissolved the higher oxide of cerium in strong HF, and dried the product at $100\text{ }^\circ\text{C}$, thus preparing the hydrated tetrafluoride $\text{CeF}_4 \cdot \text{H}_2\text{O}$. He also converted CeF_3 in CeO_2 and he used the hydrated dioxide for synthesizing the double salt $3\text{KF} \cdot 2\text{CeF}_4 \cdot 2\text{H}_2\text{O}$. Based on the existence of CeF_4 , Brauner was able to show that this element should be placed in group IV-8. It must be noted that Mendeleev came to the same conclusion on the basis of the composition CeO_2 of the higher oxide of cerium, but without conclusive experimental evidence. Brauner also continued his study of the oxide of didymium. He realized that he needed to convert it into salts if he was to prove the pentavalency of didymium. Brauner tried almost everything that came to his mind in order to form the pentafluoride, DiF_5 , as well as its double salts, but it was to no avail. His research was moreover clouded by the fact that didymium did not appear to be a genuine element, but rather a mixture of elements. Brauner discovered that even the most pure, crystalline products of didymium represented a mixture of two elements. He endeavored to purify his didymium samples by the repeated process of fractionated precipitations with oxalic acid, but he did not manage to obtain it in a pure, elementary state. Amidst all his confusing work on didymium, Brauner also attempted to redetermine the atomic weight of lanthanum, as well as to determine its place in the periodic system. After having verified the purity of his lanthanum specimens with the aid of spark spectroscopy, he ultimately concluded that there is no tetravalent lanthanum, but only trivalent lanthanum with an atomic weight of 138.27. Even though

Brauner had not yet succeeded in preparing the pentafluoride of didymium or its double salts with KF, the existence of Di_2O_5 had already been firmly established. He was very confident that it would soon turn out to be a real oxide, and he therefore thought the pentavalency of didymium a proven fact. Even though the results of his fractionated precipitations had made him question the complexity of didymium, he still believed it to be a genuine element with an atomic weight of 146.18. All these facts spoke in favor of the correctness of the Mendeleev method. Adhering to the individual placement of the rare-earth elements in successive groups, he came to the following accommodation which was in full compliance with the periodic law:

III-8	IV-8	V-8
La = 138.27	Ce = 141.60	Di = 146.18

Brauner published his first papers on the rare earths in 1881. On September 21, 1881, Brauner attended in Salzburg (Austria) the meeting of Naturalists and Doctors where he presented two papers on his rare-earth explorations and their accommodation in the periodic table. Both these papers were subsequently published in the proceedings of the Salzburg meeting (Brauner, 1881a,b) and they were also included in the *Berichte* in a summarized format (Brauner, 1882a). In December 1881, Brauner visited the Academy of Vienna where he delivered a lecture on his rare-earth research. His paper was published soon after in the journal *Monatshefte* (Brauner, 1882b) and translated into French, in *Le Moniteur Scientifique* (Brauner, 1882c). The results of his first investigations were also presented during a meeting of the Chemical Society in London on December 15, 1881, by Sir Henry Roscoe (Brauner, 1882d). Whilst Brauner's experiments were in progress, Nilson and Pettersson published a series of objections to the periodic system, one of which consisted in the statement that insurmountable difficulties presented themselves to the classification in the system of the numerous rare-earth elements (Akeroyd, 2003; Nilson and Pettersson, 1880). But Brauner objected that the results described in his paper proved that with the metals cerium, lanthanum, and didymium, this was not the case, but that, on the contrary, each of these metals was found to occupy its own characteristic position in the system. Brauner published a periodic table in which all rare-earth elements had been individually laid down; Sc in III-4, Y in III-6, La in III-8, Ce in IV-8, Di in V-8, Tb in VI-8, Er in V-9, and Yb in III-10 (Figure 9) (Brauner, 1882a). Brauner's belief in the pentavalency of didymium convinced him that all other rare-earth elements would be successfully accommodated in due time. He thus placed terbium in group VI and erbium in group V, even though their hexa- and pentavalency had not yet been demonstrated. Brauner was moreover under the impression that the

Das periodische System der Elemente.

Gruppen	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Reihen	(R X ₇) R ₉ O	(R X ₆) R ₂ O ₂	(R X ₅) R ₂ O ₂	R H ₄ R ₂ O ₄	R H ₃ R ₂ O ₄	R H ₂ R ₂ O ₆	R H R ₂ O ₇	(R ₂ H) } Verbindungs- (R ₂ O ₈) } formen
1.	1 Li							
2.	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
3.	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35.5 Cl	
4.	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56, Co 59, Ni 59, Cu 63
5.	(63 Cu)	65 Zn	69 Ga	72 ?	75 As	78 Se	80 Br	
6.	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	? 100	Ru 104, Rh 104, Pd 106, Ag 108
7.	(108 Ag)	112 Cd	114 In	118 Sn	120 Sb	126 Te	127 J	
8.	Cs 133	Ba 137	La 139	Ce 141.6	Di 146.7	Tb 148.8 ?	Sm 150 ?	? 152, ? 153, ? 154, ? 156
9.	150 ?	158 ?	? 159 Y _a ?	162 ?	166 Er?	167 ?	? 169 Tm?	
10.	? 170	? 172	Yb 173	? 177	Ta 183	W 184	? 190	Os 193 ¹⁾ , Jr 193, Pt 195, Au 197
11.	(197 Au)	200 Hg	204 Tl	207 Pb	210 Bi	? 214 Ng?	219 ?	
12.	? 221	? 225	? 230	Th 234	? 237	U 240	? 244	

¹⁾ Aus der Dampfdichte des Os O₄ (Deville und Debray, Ann. chim. phys. (3) 56, 476) ergibt sich die Zahl 193 als Atomgewicht des Osmiums.

FIGURE 9 Brauner's periodic table of 1882 with a homologous accommodation of the rare-earth elements (reproduced from Brauner, 1882a).

rare earths consisted of 19 elements, beginning with lanthanum in III-8 and ending with ytterbium in III-10. Thirteen of these elements were still unknown, according to Brauner's opinion. It therefore appears that Brauner did not accept the discoveries of samarium (by Delafontaine in 1878 and by Lecoq de Boisbaudran in 1879), holmium (by Delafontaine and Soret in 1878 and by Cleve in 1879), thulium (by Cleve in 1879), and gadolinium (by Marignac and Soret in 1880).

Brauner left Manchester during the summer of 1882 and returned to Prague where he was appointed lecturer in chemistry at Charles University. Despite Brauner's laborious efforts in the field of the rare earths, in particular his quest for the salts of pentavalent didymium, most of his results remained disappointing. The reason for this was twofold. First, Di_2O_5 appeared to be a peroxide after all, given that it could not be converted into salts and double salts. Secondly, the evidence for the complex character of didymium was mounting up. It turned out that didymium was not a genuine rare-earth element but rather a mixture of two or more rare earths.

Brauner came very close to the discovery of praseodymium and neodymium. He found that didymium could be separated in two fractions, which he called $\text{Di}\alpha$ and $\text{Di}\beta$. The fraction containing $\text{Di}\beta$ gave a black higher oxide and salts of green color. In the fraction $\text{Di}\alpha$, which gave pink-violet salts and a higher oxide of light brown shade, several absorption lines were absent, which were intensified in the $\text{Di}\beta$ fraction. Brauner had discussed this in the spring of 1882 with Roscoe and intended to call this new element "bunse-nium," in honor of Robert Bunsen. At that time appeared a communication of Cleve from Upsala (Sweden), in which this great authority in rare earths denied that didymium would be a mixture rather than a single element. Brauner was convinced that Cleve was wrong, but he decided to wait in order to be able to contradict him after having thoroughly worked out the problem. Unfortunately he postponed the publication of his work too long and finally, in 1885, Carl Auer von Welsbach in Vienna (Austria) succeeded in isolating two new elements from didymium compounds, which he called praseodymium and neodymium and which were in fact identical to the $\text{Di}\beta$ and $\text{Di}\alpha$ fractions of Brauner (1930). Brauner later on blamed von Welsbach of not having mentioned his earlier work on didymium.

In 1884, Brauner presumed that terbium and erbium would not fit into the positions VI-8 and V-9, because didymium did not fit in V-8. All his attempts to obtain the rare earths in a higher stage of oxidation had come to nothing. It thus seemed as if all rare-earth elements were trivalent (with the exception of tetravalent cerium). Brauner therefore wrote that one had to be ready to accept a number of anomalies within the eighth and ninth series of the periodic system, which could not be found in other rows. In view of the fact that the rare-earth elements were not analogous to the alkaline metals and alkaline earths in groups I and II, and due to the fact that they did not exhibit any similarity with the members of groups V, VI,

VII, and VIII (as a consequence of their failing to display valencies higher than three), Brauner had to conclude that the individual placement of the rare-earth elements (i.e., Mendeleev methodology) had failed. [Trifonov \(1963\)](#) explained this anomaly by stating that a change in the properties of the rare-earth elements along the horizontal did not agree with the change in properties along the vertical. This “horizontal anomaly” got of course more and more pronounced as the years passed and more rare-earth elements were brought to light. Unfortunately, Brauner was blinded by the *Mendeleev Method*, and he kept searching for new experimental evidence that would speak in favor of the individual accommodation of the rare earths. Only in 1902, after 25 years of fruitless endeavors, did Brauner change his view and did he propose an alternative placement for the rare-earth elements (see [Section 4.3](#)).

Brauner turned to the experimental determination of the atomic weights of the rare-earth elements. He published at least ten papers on lanthanum, cerium, praseodymium and neodymium (or didymium) during the period 1882–1903, with emphasis on the atomic weights of these elements ([Brauner, 1882e, 1883, 1885a,b, 1891, 1898a,b, 1901a,b, 1903a,b; Brauner and Batek, 1903; Brauner and Pavlicek, 1901, 1902](#)). These determinations fitted in with Brauner’s life’s aim to fix the position of the so-called *rare elements* and especially those of the rare earths in Mendeleev’s system. Indeed, by having the exact atomic weights in one’s possession, all rare earths could be ordered sequentially according to their increasing atomic weight. We cannot prevent ourselves however from raising some questions as to the usefulness of Brauner’s new research program. The difficulty of accommodating the rare earths was not caused by an erroneous, out of order sequence of rare earths, but rather by the fact that these elements did not exhibit higher valencies. It was their pronounced similarity and unique nature that was undermining the Mendeleev method. Brauner also investigated the atomic weight of tellurium, which was another anomaly in Mendeleev’s system, since its atomic weight of 128 was higher than that of iodine (127), although everyone agreed that tellurium was to *precede* iodine in the periodic table on the basis of its chemical properties. In 1888, Brauner also advocated the adoption of oxygen instead of hydrogen as the standard for calculating atomic weights ([Brauner, 1888a,b](#)). When, during that same period, a whole new group of elements was discovered (the noble or inert gases), Brauner was at first unwilling to recognize these as genuine elements ([Brauner, 1896](#)). He thus started some investigations of his own and went so far as to propose that helium might be an allotrope of hydrogen. He also put forward the claim that argon was triatomic nitrogen. As mentioned before, Brauner never lost faith in the success of the *Mendeleev Method* for accommodating the rare earths during the period 1884–1902. Thus in 1895, for example, Brauner wrote a short paper about cerium for *Chemical*

News in which he stated the following question (Brauner, 1895): “Where is there a place in the periodic system for the numberless rare-earth metals (true chemical asteroids) the atomic weight of which varies between 140 and 170?,” and he wrote:

Beryllium, Be = 9, is undoubtedly a divalent rare-earth element, with the oxide RO, as was shown by the author in 1878, 1881, and 1882. Then come the trivalent elements: scandium, Sc = 44; yttrium, Y = 89; lanthanum, La = 138; and ytterbium, Yb = 173, with the oxides, R₂O₃. Cerium, Ce = 140, forms a transition to the tetravalent earth elements, being both trivalent and tetravalent, with the oxides R₂O₃ and R₂O₄. Thorium, Th = 232, is only tetravalent with the oxide R₂O₄, though a lower oxide, Th₂O₃, may exist, corresponding to the lower oxides of niobium and tantalum. At the present limit of the periodic system and outside it rare-earth elements may be expected, possessing the oxides R₂O₅, R₂O₆, and perhaps even R₂O₇ and R₂O₈, with distinct basic properties. Very probably the atomic weight of either neodymium (R''' = 140.5) or praseodymium (R''' = 143.5) will be 235 and the oxide R₂O₅, or 282 and the oxide R₂O₆ (a true Neptune of the periodic system), for only one of both constituents of the old didymium, more probably praseodymium, yielding salts of the higher oxide, which seems to be as unstable as is CeCl₄ [. . .], will find its place in the eighth series next to cerium.

Brauner clearly held on to his conviction that all rare-earth elements could be accommodated on an individual basis in the different groups of the periodic table. Brauner therefore concluded that the valency of the rare-earth elements increased with increasing atomic weight, so that the periodicity was not undermined by the presence of the rare earths. In 1898, he repeated his claim that the pure oxides of praseodymium and neodymium would probably be found to have the formulae Pr₂O₅ and Nd₂O₆, so that the eighth series of the periodic system would assume the following form (Brauner, 1898b):

I-8	II-8	III-8	IV-8	V-8	VI-8
Cs = 133	Ba = 137.4	La = 138.2	Ce = 139.7	Pr = 141	Nd = 143.6

Despite Brauner's belief in the validity of the Mendeleev methodology, he also had to admit that he had not yet succeeded in resolving the rare-earth crisis. Thus Brauner wrote in 1901 with reference to praseodymium that its maximum valency was tetravalent, like that of cerium but that no place had been found in the periodic table for an element possessing the physical and chemical properties of praseodymium and its compounds (Brauner, 1901b). He also admitted that the difficulties of finding a place for neodymium in the periodic table were even greater than in the case of praseodymium.

At the beginning of the twentieth century, only scandium, yttrium, lanthanum, and cerium had been accommodated in the periodic system with some certainty, but all other rare earths remained homeless. As a result, more and more chemists were starting to question the strength of the periodic table. They were losing faith in the universality and the naturalness of the periodic law, and became skeptical about the dictum that all the properties of the chemical elements are periodic functions of their atomic weights. Some of them, like Nilson and Pettersson, put forward their doubts and uncertainties. The French chemist Grégoire Wyruboff (1843–1913) recognized that the periodic system was a very interesting and highly ingenious table of analogies and dissimilarities between the simple bodies, but he also noticed some problems, as for example the accommodation of the rare earths. Since the laws of nature admitted no exceptions, Wyruboff felt somewhat surprised that the periodic law was accepted (Wyruboff, 1896). He concluded that there was nothing which merits the name of law or system and claimed that the periodic law had to be rejected as a whole. He downgraded Mendeleev's system to nothing more than a *catalogue raisonné* of the elements. Wyruboff gave the following critique about the accommodation of the rare earths in the periodic table (Wyruboff, 1896):

Prof. Mendeleeff admits for the three cerite metals La = 138, Ce = 140, and Di = 192. He required this succession, since cerium yielding a higher oxide should not be placed upon the ascending branch of the curve before lanthanum. But Marignac, Bunsen, Jegel, Rammelsberg, and Wolf have found Ce = 138, with deviations not exceeding one or two units of the first decimal. Prof. Brauner alone has obtained 140 by the calcinations of the sulfate, a process absolutely defective, as Schützenberger has recently pointed out. As for lanthanum, the majority of recent determinations lead to a figure very near 138.5. Mendeleeff, to give more symmetry to his curve, selected that which presents the lowest figure. As for didymium, it is especially embarrassing for the periodic classification. In 1886 it was split up by Auer von Welsbach into neodymium (Nd = 141) and praseodymium (Pr = 143.6). Now, this latter gives on calcination an oxide higher than R_2O_3 , whence neodymium ought to be placed on the same horizontal line as lanthanum. This part of the curve would then become quite irregular, whence Mendeleeff retains in his table of 1889 the old didymium, contenting himself with asserting that the two new metals ought not to be simple bodies, and that there is no occasion to occupy ourselves with them. The arbitrary selection of oxides and of atomic weights is the gravest critique which we are justified in addressing to Prof. Mendeleeff.

In spite of the somewhat exaggerated character of Wyruboff's sharp critique, there was some truth in his statement that Mendeleev's disbelief

in the elementarity of praseodymium and neodymium was too easy an answer. As a matter of fact, it appears as if Mendeleev was starting to doubt the validity of his system as well. This was due to a number of reasons. First, there had been the discovery of the noble gases which had severely threatened the periodic law, until Errera and Ramsay, independently of each other, put forward the hypothesis to accommodate them into a whole new group of elements (group VIII or 0). Secondly, the inversed placements of tellurium and iodine; argon and potassium; and cobalt and nickel remained a mystery and thirdly, the rare-earth crisis was only growing worse. It thus seems as if Mendeleev preferred to look away from these threats, and he clearly withdrew himself more and more from the ongoing discussions. [Trifonov \(1970\)](#) very well described this change in Mendeleev's attitude towards the rare earths:

If in the first stage Mendeleev presumed the existence of a whole series of undiscovered rare-earth elements on the basis of the periodic system, in the second stage of development a majority of these elements were actually discovered and they were generally trivalent. The problem about their position in the table was, therefore, unprecedentedly serious. If in the first stage Mendeleev was actively engaged in the problem of the position of rare-earth elements in the system, discussing different versions for the position of different elements, then in the second stage his views were characterized by maximum caution.

The crux of the rare-earth problem was obvious. Despite all experimental attempts of Brauner and other chemists, the rare-earth elements refused to exhibit valencies higher than three. This implied that their properties were not regularly changing with ascending atomic weight, as was the case with all other members. The Mendeleev methodology for accommodating the rare earths had failed and nobody knew what alternative to propose. Their pronounced similarity baffled the whole chemical community, and everyone wondered how these resemblances could be explained, and whether this explanation could help in solving the problematic accommodation of the rare earths in the periodic table.

It should be mentioned here that there had been a close contact between Mendeleev and Brauner via correspondence ([Brauner, 1930](#); [Kedrov and Chentsova, 1955](#)). The correspondence between Brauner and Mendeleev is of great historical interest. Its content clearly demonstrates how these two chemists mutually influenced each other during the period 1881–1907, and it provides us with new insights into Brauner's rare-earth research. Luckily, Mendeleev was a very orderly man, who carefully maintained even the most minor notes and letters which he received from others, especially when the content of these letters was related to his scientific activities. Mendeleev brought all these letters

together in chronological order and he carefully pasted them in large albums, which are currently stored in the Mendeleev Museum and Archive in his university apartment in St. Petersburg. Most of Brauner's letters were as such pasted down in Mendeleev's albums. The first part of their correspondence, covering the period 1881–1888, consisted of more than 20 letters. One can conclude on the basis of Mendeleev's response that Brauner had written Mendeleev in his first letter about his wish to further investigate the rare-earth elements, pointing out the importance of the higher oxide of didymium. Mendeleev's cordial reply was dated February 8, 1881 (according to the Gregorian calendar). Mendeleev also wrote of the rare earths and their problematic accommodation in the periodic table. He was happy to offer Brauner the following advice (Brauner, 1930):

If you have begun to work on rare elements, allow me to direct your attention to the fact, that the solution of all is to be looked for in didymium, which is little known and even this little not exact. It is didymium which is the most interesting. Seven years ago I worked at it, but I have not published anything; yet I think, judging from the number of the bodies, that in its higher form of oxidation didymium gives salts, and that the ordinary compounds of didymium are mixtures, that they are not pure. If you like I shall send you the oxide of didymium I possess (may be I have about 80 g) for your work. I have also much of zircon, the mineral from Ural, which I can offer you if it will help your research. I have little of gadolinites; yet my determination of the atomic weight of yttrium was proved by later works.

Mendeleev ended his letter by repeating once more that he was delighted to know that the periodic system had got a defender like Brauner. Brauner was particularly pleased by Mendeleev's letter because it confirmed his own views about the rare-earth elements. Brauner gladly accepted Mendeleev's offer to send him samples of didymium oxide and some other rare-earth specimens. He reported to him that he had been experimenting with the higher oxide of didymium since 1878 and meticulously described his experimental endeavors of the last four years. In his letter of February 23, 1881, Mendeleev agreed that the higher oxide of didymium was especially important and confessed that he had himself thought of it and directed his research to this problem.

4.2 Meta-Elements

Bohuslav Brauner had approached the rare-earth crisis from a traditional chemical point of view. Both the search for higher valencies and complicated atomic weight determinations had been central to his research during the last quarter of the nineteenth century, but neither of these methodologies allowed to prove the validity of the homologous accommodation. Brauner's adherence to the *Mendeleev method* had led him to a

dead end and a change was called for. Not the classical techniques of chemical analysis, but the novel methods of spectroscopic investigation came to the rescue of the rare-earth specialists. Bunsen and Kirchhoff had built their first spectroscope in 1859. The usefulness of this instrument was established a few months later, when the two German scientists discovered a novel element, cesium. Another alkaline metal, rubidium, was discovered by Bunsen in 1861, and Sir William Crookes (1832–1919, [Figure 10](#)) spoke about the existence of a new element, which he named thallium during that same year. Reich and Richter discovered indium in 1863 and Lecoq de Boisbaudran tracked down Mendeleev's eka-aluminium (i.e., gallium) in 1886. Throughout these 30 years, spectroscopic research had yielded rich rewards, and many new elements had been characterized by their unique spectrum.

During his research on electrical discharges in cathode ray tubes in the late 1870s, Sir William Crookes noticed that a large number of substances emitted phosphorescent light when they were exposed to a discharge by means of an induction coil in a highly exhausted vacuum tube ([Brock, 2008](#)). Some substances emitted light of the greatest intensity, while others showed only a faint phosphorescence. Still others showed no sign of phosphorescence at all. He found that diamond had the most brilliant

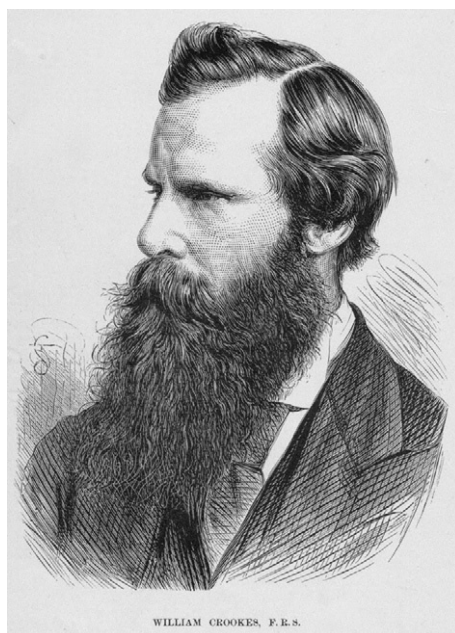


FIGURE 10 Sir William Crookes (1832–1919). Photo and permission from Edgar Fahs Smith Collection.

phosphorescence intensity, followed by ruby. When this phosphorescent light was examined with the aid of a spectroscope, it turned out that most bodies gave out continuous spectra, but sometimes the spectrum of the phosphorescent light was discontinuous, and a number of beautifully colored spectrum lines or bands appeared on the dark background. Crookes' attention in the early 1880s was directed towards these latter bodies, and he called the study of their spectra *radiant matter spectroscopy* (Crookes, 1879, 1884a,b; DeKosky, 1973). Crookes was convinced of the possibility of correlating the observed bands with known and unknown elements, just as he had been able to discover a new element, thallium, during his spectroscopic researches in 1861. He started to investigate the spectra of the rare earths (Crookes, 1884a,b, 1886f,g,h,i,j, 1889b). After Crookes had characterized the spectra of yttrium and samarium, his attention was drawn by a mysterious orange spectral line. The anomalous line did not come from yttrium or samarium, and Crookes therefore postulated the existence of a new element. This was a bold hypothesis. Chemical elements were usually characterized by a unique spectrum of bands and lines, but this time Crookes claimed that he had demonstrated the existence of a new element, based on a single spectral line.

The repeated chemical fractionations of yttrium resulted in mysterious changes in its spectrum. Finally, Crookes was able to obtain a number of fractions and each fraction gave a spectrum which corresponded with one line of the spectrum of yttrium. In analogy with the orange line, Crookes considered this as an indication of the existence of new elements. Yttrium did no longer meet the criteria of homogeneity and elementarity and it appeared to consist of seven constituents (Crookes, 1886k). Crookes speculated that all chemical elements could be split into a number of constituents by advanced fractionations. Because this hypothesis was steadily increasing the number of elements, Crookes developed his famous concept of *meta-elements* (Crookes, 1888a,b,c,d,e). According to Crookes, the term *element* had to be replaced by the term *elemental group*. Each element was made up of a collection of *meta-elements* (or *elementoids*). These meta-elements differed slightly from each other in their atomic weight, chemical and physical properties. Crookes had thus succeeded in splitting the element yttrium in seven meta-elements. He stated that the atomic weight which was ascribed to yttrium merely represented a mean value around which the actual weights of the individual atoms of the "element" range within certain limits. According to Crookes chemical fractionation was the method par excellence to split an elemental group in its meta-elements (Crookes, 1886a,b,c,d,e).

Crookes' radiant matter spectroscopic research on the rare earths seemed to point towards the complexity of the elements. It thus provided an excellent empirical basis for his influential lecture "On the nature and the probable, or at least possible, origin of the so called elements" which

he presented during his presidential address before the Chemical Section of the British Association on September 2, 1886 (Crookes, 1886b). The epistemological nature of the elements was considered one of the greatest riddles for the chemical sciences throughout the nineteenth century. Many chemists had attempted to unravel the secret composition of the so-called elements, but all had been in vain. Since the chemical revolution in 1789 and the pioneering research of Antoine Laurent Lavoisier (1743–1794), chemical elements had been defined as the endpoint of chemical analysis. But according to Crookes' opinion, all these traditional operational definitions were worthless. There was a complete uncertainty about the elementary character of the chemical elements, and nothing prevented chemists from putting forward the hypothesis that the chemical elements might turn out to be composite bodies after all. As a matter of fact, many renowned chemists and physicists, e.g., Faraday, Stokes and Graham had played with the idea of complex elements. Crookes started his lecture by mentioning the most famous hypothesis concerning the ultimate constituents of the elements which had been suggested by Prout in 1816. According to Prout's hypothesis, all chemical elements were complex aggregates of hydrogen since their atomic weights were all approximate multiples of the atomic weight of hydrogen. A more complete agreement between the hypothetical (theoretical) and practical atomic weights could be obtained by assuming that the *protyle* (i.e., a hypothetical primitive substance from which the chemical elements were supposed to have been formed) was not hydrogen, but a half or fourth part of the hydrogen atom or another simple substance of low atomic weight. Although Crookes had repeatedly spoken about the possible complexity of the elements, he nevertheless had to admit that not even the highest temperatures or the most powerful electric currents had been able to dissociate the chemical elements.

Crookes was also convinced that the chemical elements had evolved out of some primordial and rudimentary form of matter via a *process of genesis* (Crookes, 1887, 1889a). Laplace's cosmological theories about the evolution of the heavenly bodies as well as Darwin's recently published work "On the Origin of Species" inspired Crookes to compare the periodic kingdom of elements with the organic world of fauna and flora, a comparison first made by the astrophysicist Norman Lockyer (1836–1920) (Leone and Robotti, 2000, 2003). Both kingdoms were seen as the outcome of a process of evolutionary development which had been subjected to the laws of nature. The concerted action of a struggle for existence and the survival of the fittest had determined which elements survived and which became extinct. Crookes noticed that both elements and animals display species that are common and species that are rare. The analogy could not be pushed too far however, since there was no fossil record of extinct elements. The mineral kingdom, on the other hand, pointed towards the genesis of the elements as well. The heterogenous distribution of the

elements in the earth's crust had puzzled both geologists and chemists. An explanation for the simultaneous occurrence of sodium and chlorine, or lead and sulfur (as sodium chloride and lead sulfide) could be given on the basis of their opposite chemical affinities. But Crookes also mentioned the grouped occurrence of strongly related elements that showed absolutely no affinity for each other, such as nickel and cobalt, the two platinum groups, and the rare-earth elements. It appeared more logical to claim that these elements had been formed under nearly identical circumstances during the genesis of the elements.

This elemental evolution, according to Crookes' opinion, began at extremely high temperatures and ultra gaseous conditions. Atoms had not yet formed in the beginning of time, and only the *protyle* permeated throughout the universe. But as time progressed, the *protyle* cooled down and all rudimentary matter started to granulate until the first atoms were formed. This condensation process could result in atoms of all possible weights, but since hydrogen (or perhaps helium) was the simplest element from a structural point of view, this element was created first during the agglomeration of the *protyle*. Soon after, as the temperature had lowered a little more, a second element of greater atomic weight was formed. As a result, each element evolved from the *protyle* at a well defined temperature. The longer this temperature of formation was sustained (i.e., the slower the cooling rate at that region of temperatures), the sharper defined the resulting element. For instance, hydrogen, oxygen, and other clear cut elements had all been formed during these long periods of slow cooling. At irregular rates of cooling, on the other hand, less defined elements were produced. A stage of rapid cooling thus caused the formation of groups of closely related elements, such as the transition metal triads with very similar atomic weights. At certain times during the evolutionary history of the elements, the temperature dropped even faster and the set of rare-earth elements was formed. This evolutionary process did not only determine the birth of each element, it also established their atomic weights, affinities and chemical positions in the periodic table. Crookes thought the cooling process had never been slow enough to create elements with atoms of identical weight, and postulated that the atomic weights merely represented a mean value around which the actual atomic weights of the atoms varied within certain narrow limits.

All these statements seemed of course very bold and hypothetical at first sight, but Crookes knew he could provide his daring and provocative thesis about the complexity and genesis of the elements with a scientific underpinning, thanks to his rare-earth research. In 1886 Crookes drew up an alternative representation of the periodic table, his *Mighty Pendulum* (Figure 11), in which he modeled a possible scenario of elementary evolution (Crookes, 1886). This format was inspired by Reynolds' "Note on a Method of Illustrating the Periodic Law" (Reynolds, 1886). In order to fully grasp the meaning of this new table layout, it is constructive to

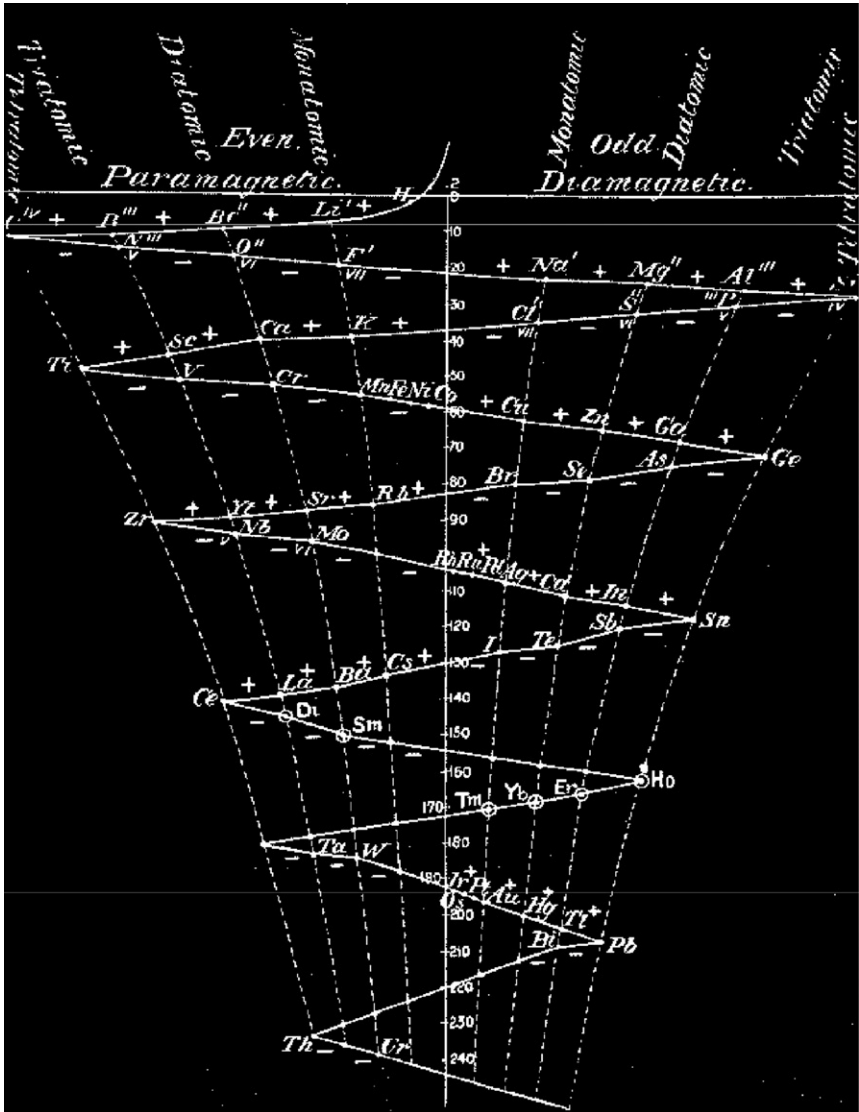


FIGURE 11 Crookes' mighty pendulum of 1886. Reproduced from [Crookes \(1886\)](#).

consider the first period of the periodic table, {Li, Be, B, C, N, O, F}. The properties of the elements change step by step according to a gradual transition from lithium to fluorine. The first element of a given period therefore stands in sharp contrast with the last one. The next step from fluorine to sodium moreover happens *per saltum* according to an abrupt transition since sodium is again an alkaline metal. A point of mean

variation can consequently be found in the middle of each period with carbon and silicon as representatives of the class of the so-called *meso-elements*. The triad of elements to the right of a given *meso-element* consists of electropositive members, while the elements to the left are all electronegative. The elements at opposite sides of a *meso-element* form pairs of elements with analogous valencies:

	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19
<i>Valency</i>	1	2	3	4	3	2	1

All this could be represented by some sort of zigzag curve, but Crookes slightly altered Reynolds' diagram and he presented the periodic law as a *mighty pendulum* with the *meso-elements*—carbon, silicon, titanium, germanium, etc.—situated at the apex of each pendulous swing. In between these tetratomic elements lay the monatomic, diatomic and triatomic elements with valencies 1, 2, and 3 respectively. All elements could be uniquely determined by the Cartesian coordinate system in which the abscissa denoted the combining capacity of the element in question, whilst the ordinate represented its atomic weight. Gaps alluded to the possible existence of undiscovered elements. Thus the elemental evolution started at the top of Crookes' mighty pendulum and ended with the formation of thorium and uranium, at the bottom of the diagram. The zigzag curve moreover suggested the presence of two forces, acting simultaneously on the original *protyle* in both the vertical and the horizontal direction. The first creative force represented time and was tied up with a sinking of the temperature from the dissociation point of hydrogen down to the dissociation point of the heaviest elements. The horizontal force periodically oscillated from left to right and was connected with electricity, the vertical axis representing neutrality. The further removed from this neutral center line, the greater the atomicity of the elements concerned. Paramagnetic elements were formed at the left hand side of the center line; diamagnetic elements on the right hand side. On approaching the center line, electronegative elements were formed. Electropositive elements, conversely, came into being on the retreating halves of the pendulous swing. In 1888, Crookes decided to alter the *mighty pendulum* to his *vis generatrix* by attempting to project the plane pendulum into three dimensions and considered a figure of eight or lemniscate the best representation of his zigzag diagram since it allowed the curve to pass twice through the neutral point in each cycle (Figure 12) (Crookes, 1888a, 1898). Crookes' viewpoints threw considerable light upon the outlandish nature of the transition metals, and the concept of meta-elements greatly facilitated the development of alternative accommodation methodologies for the rare-earth elements (*vide infra*).

Neither Crookes' *mighty pendulum* (Crookes, 1886l) nor his *vis generatrix* (Crookes, 1888a, 1898) had offered an alternative accommodation for

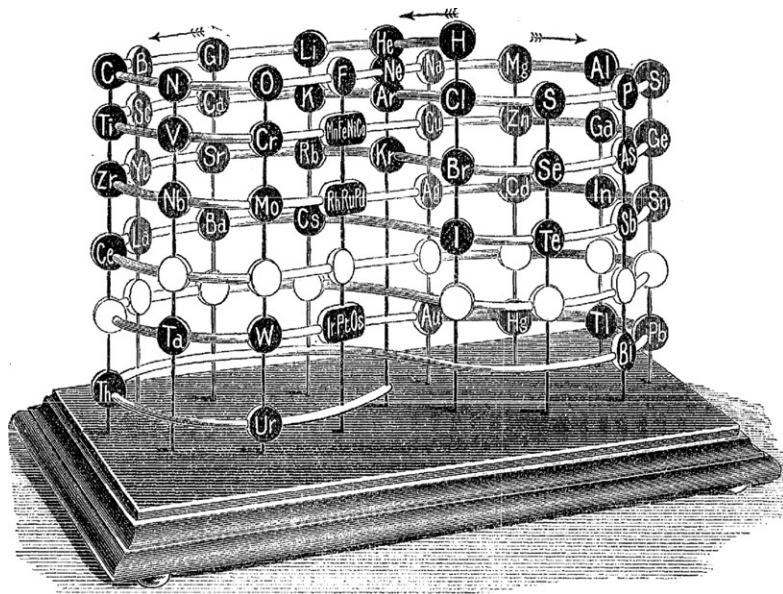


FIGURE 12 Model of Crookes' vis generatrix of 1898—built by his assistant, Gardiner. The vertical scale represents the atomic weight of the elements from H = 1 to Ur = 239. Missing elements are represented by a white circle. Similar elements appear underneath each other (reproduced from Crookes, 1898).

the set of chemical elements. Both systems differed from Mendeleev's 1871 table in their peculiar two- and three-dimensional layout, but the placement of the elements in primary and secondary groups, short and long periods, odd and even series, had remained the same. Crookes, most valuable contribution to the development of the periodic system consisted in providing a reasonable explanation of the periodic law by means of its relation with the unity of matter and inorganic evolution. The peculiar accommodation of the transition metals, however, needs some further consideration. Crookes had located the triplets (iron, nickel, cobalt), (rhodium, ruthenium, palladium), and (osmium, iridium, platinum) as three independent groups near the center line of his mighty pendulum (Figure 11). When the pretzel-shaped model of the periodic law was drawn up two years later, Crookes did not hesitate to cluster the transition metals once again as three triads near the neutral axis (Figure 12). He called these elements *interperiodic*, both because their atomic weights excluded them from the small periods into which the other elements fell, and because their chemical relations with certain members of the adjacent periods showed that they were probably interperiodic in the sense of being transitional. Crookes' interperiodic accommodation methodology was therefore identical with the one advocated by Mendeleev in his paper

of 1871. It must moreover be observed that Mendeleev had chosen to overcrowd the boxes of his eighth group with sets of four elements each, instead of accommodating the transition elements in four different boxes. Thus one finds in his 1871 table, at the end of the fourth series, a tetrad of elements (iron, cobalt, nickel, and copper), occupying just one position, in complete analogy with Crookes' collective grouping of these metals between manganese and copper in his zigzag curve.

Both Mendeleev and Crookes were thus accused of violating the concept of single occupancy, by placing more than one element in the same position of the periodic table. One recalls however that Crookes had offered a way out in his papers on the complexity of the elements, given the fact that he proclaimed that the members of each triplet had to be regarded as modifications of one single form of matter. He did not consider the closely related elements platinum, osmium, and iridium to be genuine elements, but rather looked upon them as constituents of one single transition element. According to Crookes' terminology, platinum, osmium, and iridium had to be regarded as meta-elements of one elemental group. Consequently, there was no more a violation of the concept of single occupancy as with all other elements (i.e., elemental groups), since Crookes was accommodating just one elemental group in the case VIII-10. Would it not be justified according to this line of reasoning to consider the even more closely allied rare-earth elements as meta-elements of one elemental group? Would it not be tempting to collectively cluster these trivalent elements in one case of the periodic system, according to a so-called *intraproductic accommodation methodology*? Quite surprisingly, Crookes did not adhere to this method and he preferred to place the rare earths as ordinary elements throughout the higher periods of his mighty pendulum. In spite of this, Crookes had encircled most of the rare-earth elements, meaning that they were out of place, owing to their atomic weights not having been correctly determined. He also thought that several rare-earth elements still had to be discovered. Crookes did not put his ideas into action and decided not to include the rare-earth elements in his *vis generatrix* (with the exception of lanthanum and cerium), but his proposal would soon be taken up by the Bohuslav Brauner, who was still struggling with the problematic accommodation of the rare earths.

4.3 Asteriod Hypothesis

In a lecture at the 11th Congress of Russian Natural Scientists in St. Petersburg in 1902, Brauner proposed a completely different accommodation methodology for the rare earths according to which all rare earths had to be put in the fourth group. Brauner termed this idea the *asteroid hypothesis*, because just as the entire group of asteroids occupies an

orbit in the solar system on which normally one single planet would be expected to move, exactly in the same way does the entire group of elements known as the rare earths occupy one single place in the system which would have been ordinarily occupied by a single element (Brauner, 1902). According to Brauner's opinion, chemists tended more and more to the idea that chemical elements were composed of some primordial matter. He thus imagined that the condensation of the *Ursubstanz* (i.e., primary matter) had not proceeded as far during the formation of the rare earths as in the other elements and concluded that it would be best to accommodate them in one and the same place in the fourth group and eighth row of the periodic system, where only cerium had hitherto been located. He provided his hypothesis with a more solid ground on the basis of the pronounced similarities among the rare earths and the fact that they all exhibited approximately equal atomic volumes in the free state. The eighth row would therefore proceed as shown in Figure 13.

Brauner naturally wondered whether one still had to presuppose the existence of analogues of niobium, molybdenum, manganese, and the three platinum metals in V-8, VI-8, VII-8, and VIII-8 respectively, and he also doubted whether the ninth row would ever be filled by seven more heavy elements. He preferred to consider the rare earths as forming a direct transition from tetravalent cerium to pentavalent tantalum. Brauner was also tempted to draw an analogy between the rare-earth elements and the transition metals since both types of elements had been collectively placed in one "pigeonhole" of the system (*interperiodically* in the case of the transition metals, and *intraperiodically* in the case of the rare earths). Brauner pushed the analogy even further on the basis of their oxide forms. Theoretically, the limiting degree of oxidation for the transition metals was RX_8 , but only osmium and ruthenium exhibited these forms of oxidation (i.e., OsO_4 en RuO_4). Similarly, the highest form of oxidation for the rare-earth elements had to be RX_4 , but this was only manifested in the oxides of cerium and praseodymium. It thus appears that Brauner had reached the same conclusions in 1902 as Mendeleev had in 1869 with regard to the transitional function of the primary groups and the rare earth – transition metal analogy.

Cs = 133	Ba = 137.4	La = 139.0	Ce = 140.2	–?	–?
			Pr = 141		
			Nd = 144		
			Sm = 148		
			Eu = 151		
			Gd = 156		
			etc.		

FIGURE 13 Position of the rare earths in the periodic table according to Brauner's asteroid hypothesis.

Instead of writing all rare earths underneath each other in IV-8, Brauner thought it more convenient to write them next to each other in groups of four, as with the transition elements (Figure 14). An even more compact method of representation consisted of writing “Ce etc. 140–178” in the case IV-8 of the periodic table (Figure 15). There were a number of interesting advantages connected with this type of accommodation. First of all, the periodicity was no longer undermined by the presence of the rare earths. Secondly, the astonishing similarities in the chemical and physical properties of the rare earths were accentuated by the placement of these metals in one case only. Finally, Brauner made it clear that the gap between La and Ta would be filled by rare earths and rare earths only. He thus delineated the boundaries of the rare-earth family.

One could be inclined to conclude that Brauner had been heavily influenced by the concept of Crookes' meta-elements when he proposed his asteroid hypothesis in 1902 (Stewart, 1909). After all, a violation of the concept of single occupancy could only be avoided by assuming the rare-earth elements to be constituent meta-elements of one and the same rare-earth elemental group. The link between Brauner and Crookes could be further substantiated by the following clues and indications. First of all, Brauner was tempted to compare the rare-earth elements with the asteroids of the solar system, in complete analogy with Crookes, who had referred to this class of metals as “the asteroids among the elements” (Crookes, 1886). Secondly, Brauner tried to provide his asteroid hypothesis with a scientific underpinning by imagining the condensation of the *Ursubstanz* during the formation of the rare-earth elements, just as Crookes had done in his lectures of 1886–1888. More than that, Brauner actually referred to Crookes in a footnote when he was writing about the primordial *Ursubstanz*. Finally, the two rare-earth specialists knew each other personally from the time when Brauner was working in Manchester, and they corresponded a lot during their lifetime. However, the influence of Crookes' concept of meta-elements should not be pushed too far. First of all, Brauner had spoken for the first time about the “confusion in this area of the chemistry of asteroids” in a letter to Mendeleev, dated February 17, 1881 (i.e., five years before Crookes' presidential address of 1886). Secondly, when he spoke about *die Kondensation der Ursubstanz*, Brauner at first referred to one of his own lectures, claiming that he had proposed this evolutionary hypothesis for the first time before the *Chemical Society of London* in March 17, 1898. How could Brauner maintain his priority if Crookes had developed his viewpoints on the epistemological nature of the concept of elements 10 years earlier, during the period 1886–1888? As a matter of fact, Brauner did not make any reference to this trilogy of papers, but he relegated his reading public to Crookes' paper of June 9, 1898 “On the Position of Helium, Argon, and Krypton in the Scheme of Elements” (Crookes, 1898). Apparently,

A. Periodisches System der Elemente (volle Gestalt).

Reihe	Gruppe 0	Gruppe I	Gruppe II	Gruppe III	Gruppe IV	Gruppe V	Gruppe VI	Gruppe VII	Gruppe VIII			
	—	—	—	—	RH ₄	RH ₃	RH ₂	RH	—			
	R	R ₂ O	RO	R ₂ O ₃	RO ₂	R ₂ O ₅	RO ₃	R ₂ O ₇	RO ₄			
1		1 H										
2	He 4	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19				
8	20 Ne	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35.5 Cl				
4	A 40	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 59	Cu 63
5		63 Cu	65 Zn	70 Ga	72 Ge	75 As	79 Se	80 Br				
6	Kr 82	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	—100	Ru 102	Rh 108	Pd 106	Ag 108
7		108 Ag	112 Cd	114 In	119 Sn	120 Sb	128 Te	127 J				
8	Xe 128	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd 144	—145				
					—147	Sm 148	Eu 151	—152				
					—155	Gd 156	—159	—160				
					Tb 163	Ho 165	Er 166	—167				
					Tm 171	Yb 173	—176					
					—178	Ta 182	W 184	—190	Os 191	Ir 193	Pt 195	Au 197
9		197 Au	200 Hg	204 Tl	207 Pb	209 Bi	212—	214—				
10	—218	—220	Rd 225?	—230	Th 233	—235	U 239					

FIGURE 14 Brauner's periodic table of 1902 with an intraperiodic accommodation of the rare-earth elements (long form). Reproduced from Brauner (1902).

B. Periodisches System der Elemente (abgekürzte Form).

Reihe	Gruppe 0	Gruppe I	Gruppe II	Gruppe III	Gruppe IV	Gruppe V	Gruppe VI	Gruppe VII	Gruppe VIII
	—	—	—	—	RH ₄	RH ₃	RH ₂	RH	— Höchste Wasserstoffverbindungen
	R	R ₂ O	RO	R ₂ O ₃	RO ₂	R ₂ O ₅	RO ₃	R ₂ O ₇	RO ₄ Höchste Oxyde
1		1 H							
2	He 4	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	Erste kleine Periode
3	20 Ne	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35.5 Cl	Zweite kleine Periode
4	A 40	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56 Co 59 Ni 59 Cu 68
5		63 Cu	65 Zn	70 Ga	72 Ge	75 As	79 Se	80 Br	Erste große Periode
6	Kr 82	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	—100	Ru 102 Rh 103 Pd 106 Ag 108
7		108 Ag	112 Cd	114 In	119 Sn	120 Sb	128 Te	127 J	Zweite große Periode
8	Xe 128	Cs 133	Ba 137	La 138	Ce etc. 140—178	Ta 182	W 184	—190	Os 191 Ir 193 Pt 195 Au 197
9		197 Au	200 Hg	204 Tl	207 Pb	209 Bi	212—	214—	Dritte große Periode
10	—218	—220	Rd 225?	—230	Th 233	—235	U 239		
									Vierte große Periode

FIGURE 15 Brauner's compact periodic table of 1902 with an intraperiodic accommodation of the rare-earth elements. Reproduced from Brauner (1902).

Brauner was completely unaware of the existence of Crookes' 1886–1888 lectures. This also explains why Brauner never mentioned the terms meta-elements and elemental groups in his 1902 paper. Indeed, the asteroid hypothesis of Brauner could be approved on the basis of Crookes' concept of meta-elements, but Brauner himself did never take this step.

4.4 Intraperiodic Accommodation Methodologies

Brauner's asteroid hypothesis is an *intraperiodic accommodation methodology* (Brauner, 1902). The rare earths are considered as forming a special intraperiodic group and they are collectively clustered in one of the groups of the periodic system. Although the asteroid hypothesis is credited to Brauner, the original idea to compare the accommodation of the rare earths with the placement of the asteroids in the solar system did not come from Crookes' papers, and neither did it come from Brauner's creative mind. About seven years before Brauner's lecture of 1902, an article from Retgers (1895) had appeared in the *Zeitschrift für physikalische Chemie*, entitled "Über einige Änderungen im periodischen System der Elemente" (On some Modifications in the Periodic System of Elements). On the second page of his paper, Retgers mentioned the group of planetoids, which occurred between Mars and Jupiter in the planetary system, and which occupied the orbit of one planet. Not surprisingly, Retgers adhered to an intraperiodic accommodation methodology and he clustered La, Ce, Di, Sm, Er and Yb in one and the same spot of the periodic system (Figure 16). It therefore seems more correct to speak about the *asteroid hypothesis of Retgers*. As a matter of fact, the whole idea of clustering the rare earths in one pigeonhole appears to have been in the air of science, since a whole spectrum of articles about the periodic table emerged at the dawn of the twentieth century, every one of them putting forward the same asteroid like hypothesis and claiming that it provided the long sought after solution for the rare-earth crisis.

Thus, Biltz devised a periodic table in 1902 where Mn, Fe, Co, and Ni were grouped together, as well as Ru, Rh, Pd; Os, Ir, Pt; and the rare earths La, Ce, Pr, Nd (Figure 17) (Biltz, 1902). He named each group after the best known member and symbolized the clusters by the summation symbol Σ . The iron group ΣFe , the palladium group ΣPd , and the platinum group ΣPt , were all located in group VII. The cerium group ΣCe , on the other hand, was placed among the trivalent elements in group III. Some authors preferred to treat the rare earths as an *intermediate group* and located them in both the third and fourth group of the periodic system. Rudorf (1903) and Benedicks (1904) (Figure 18) adhered to this type of accommodation when they published their periodic tables in 1903 and 1904 respectively. The German chemist, Stefan Meyer proposed a similar placement of the rare-earth elements in 1918 (Figure 19). Several textbook authors too were

I	II	III	IV	V	VI	VII
einwertig	einwertig	zweiwertig	dreiwertig	vierwertig	dreiwertig	zweiwertig
<i>H</i>	<i>Li</i>	<i>Be</i>	<i>Bo</i>	<i>C</i>	<i>N</i>	<i>O</i>
<i>Fl</i>	<i>Na</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>
<i>Cl</i>	<i>K</i>	<i>Ca</i>	<i>Sc</i>	<i>Ti</i>	<i>V</i>	<i>Cr, Mn, Fe, Co, Ni</i>
	<i>Cu</i>	<i>Zn</i>	<i>Ga</i>	<i>Ge</i>	<i>As</i>	<i>Se</i>
<i>Br</i>	<i>Rb</i>	<i>Sr</i>	<i>Y</i>	<i>Zr</i>	<i>Nb</i>	<i>Mo, Ru, Rh, Pd</i>
	<i>Ag</i>	<i>Cd</i>	<i>Jn</i>	<i>Sn</i>	<i>Sb</i>	<i>Te</i>
<i>J</i>	<i>Cs</i>	<i>Ba</i>	<i>La, Ce, Di, Sm, Er, Yb</i>		<i>Ta</i>	<i>W, Os Ir, Pt</i>
	<i>Au, Hg, Tl</i>	<i>Pb</i>			<i>Bi</i>	<i>Th, U.</i>

FIGURE 16 Periodic Table of [Retgers \(1895\)](#) with an intraperiodic accommodation of the rare earths. Reproduced from [Retgers \(1895\)](#).

Periodensystem der Elemente.

He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	Cl
Ar	K	Ca	Sc	Ti	V	Cr	Σ Fe
Kr	Cu	Zn	Ga	Ge	As	Se	Br
X	Rb	Sr	Y	Zr	Nb	Mo	Σ Pd
	Ag	Cd	Jn	Sn	Sb	Te	J
	Cs	Ba	Σ Ce		Ex		
	Au	Hg	Yb	Pb	Ta	W	Σ Pt
			Tl	Th	Bi	U	

Untergruppen.

Σ Ce = La	Ce	Pr	Nd	Σ Fe = Mn	Fe	Co	Ni
				Σ Pd = Ru	Rh	Pd	
				Σ Pt = Os	Ir	Pt	

FIGURE 17 Periodic Table of [Biltz \(1902\)](#) with an intraperiodic accommodation of the rare earths. Reproduced from [Biltz \(1902\)](#).

	O	I	II	III	IV	V	VI	VII	VIII
		H							
1	He	Li	Be	B	C	N	O	F	
2	Ne	Na	Mg	Al	Si	P	S	Cl	
3	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe, Co, Ni
4		Cu	Zn	Ga	Ge	As	Se	Br	
5	Kr	Rb	Sr	Y	Zr	Nb	Mo	—	Ru, Rh, Pd
6		Ag	Cd	In	Sn	Sb	Te	J	
7	Xe	Cs	Ba	[La, Ce... Yb]		Ta	W	—	Os, Ir, Pt
8		Au	Hg	Tl	Pb	Bi	—	—	
9	—	—	Ra	—	Th	—	U	—	

FIGURE 18 Periodic Table of Benedicks (1904) with an intraperiodic accommodation of the rare earths. Reproduced from Benedicks (1904).

Tabelle I. Periodisches System der Elemente.

		I								0							
		H								He							
		1.008								4.00							
		1								2							
Wertigkeit bez. Gruppennummer Symbol Atom-Gewicht Ordnungszahl (Kernladung)	1	I	II	III	IV	V	VI	VII	0	I	II	III	IV	V	VI	VII	0
	2	Li	Be	B	C	N	O	F	Ne	Li	Be	B	C	N	O	F	Ne
	3	6.94	9.1	11.0	12.0	14.0	16.0	19.0	20.2	3	4	5	6	7	8	9	10
	4	Na	Mg	Al	Si	P	S	Cl	Ar	Na	Mg	Al	Si	P	S	Cl	Ar
	5	23.0	24.3	27.1	28.3	31.0	32.1	35.5	39.9	11	12	13	14	15	16	17	18

Die Atomvolumina nehmen von der Mitte nach beiden Seiten zu.

	I	II	III	IV	V	VI	VII	VIII	I	II	III	IV	V	VI	VII	0																																																	
4	K 39.1 19	Ca 40.1 20	Sc 45.1 21	Ti 48.1 22	V 51.0 23	Cr 52.0 24	Mn 54.9 25	Fe 55.8 26	Co 58.9 27	Ni 58.7 28	Cu 63.6 29	Zn 65.4 30	Ga 69.9 31	Ge 72.5 32	As 75.0 33	Se 79.2 34	Br 79.9 35	Kr 82.9 36																																															
5	Rb 85.5 37	Sr 87.6 38	Y 88.7 39	Zr 90.6 40	Nb 93.5 41	Mo 96.0 42	?	Ru 101.2 44	Rh 102.9 45	Pd 106.7 46	Ag 107.9 47	Cd 112.4 48	Jn 114.8 49	Sn 118.7 50	Sb 120.2 51	Te 127.5 52	J 126.9 53	X 130.2 54																																															
6	Cs 132.8 55	Ba 137.4 56	seltsame Erden 139.0 bis 178 57 bis 72		Ta 181.5 73	W 184.0 74	?	Os 190.9 76	Ir 193.1 77	Pt 195.2 78	Au 197.2 79	Hg 200.6 80	Tl 204.0 81	Pb 207.2 82	Bi 208.0 83	Po 210 84	?	Em 222 86																																															
7	?	Ra 226.0 88	Ac 89	Th 232.1 90	Bv 234 91	U 238.2 92	<table border="1"> <tr> <td>La</td><td>Ce</td><td>Pr</td><td>Nd</td><td>?</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tu I</td><td>Ad</td><td>Cp</td><td>Tu II</td> </tr> <tr> <td>138.0</td><td>140.3</td><td>140.9</td><td>144.3</td><td>?</td><td>150.4</td><td>152.0</td><td>157.3</td><td>158.9</td><td>162.5</td><td>163.5</td><td>167.3</td><td>168.9</td><td>173.5</td><td>175.0</td><td>-</td> </tr> <tr> <td>57</td><td>58</td><td>59</td><td>60</td><td>61</td><td>62</td><td>63</td><td>64</td><td>65</td><td>66</td><td>67</td><td>68</td><td>69</td><td>70</td><td>71</td><td>72</td> </tr> </table>											La	Ce	Pr	Nd	?	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu I	Ad	Cp	Tu II	138.0	140.3	140.9	144.3	?	150.4	152.0	157.3	158.9	162.5	163.5	167.3	168.9	173.5	175.0	-	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
La	Ce	Pr	Nd	?	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu I	Ad	Cp	Tu II																																																		
138.0	140.3	140.9	144.3	?	150.4	152.0	157.3	158.9	162.5	163.5	167.3	168.9	173.5	175.0	-																																																		
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72																																																		

FIGURE 19 Periodic Table of Meyer (1918) with an intraperiodic accommodation of the rare earths. Reproduced from Meyer (1918).

quick at adopting Brauner's asteroid hypothesis. The first editions of the books of Jones (1903) and Smith (1906) both accommodated the rare earths in group IV of the periodic system. Ostwald (1904), on the other hand, preferred to cluster the rare earths in group III. Six more textbook authors converted to the intraperiodic accommodation methodology during the

period 1914–1921. [Arnold in 1914](#), [Newell in 1916](#), [Walker in 1919](#), and [Holmyard in 1922](#) located the rare earths in group IV. [Friend et al. \(1917\)](#), on the other hand, chose group III, and [Norris in 1921](#) opted for a grouped accommodation in the groups II, III, and IV.

5. NIELS BOHR AND HENRY MOSELEY

5.1 Bohr's Atomic Theory

Thomson's model of the atom could not provide an explanation for the large angle deflections of α particles as first observed in the laboratory of Rutherford (1871–1937) in Manchester. Rutherford consequently improved Thomson's model by postulating the existence of a central nucleus in 1911. He thus provided an explanation for the anomalous scattering phenomena, but he realized that his nuclear model was unstable according to the doctrines of classical physics. The permanent radiation remained a problem until the summer of 1912, when Niels Bohr (1885–1962, [Figure 20](#)) provided a solution on the basis of his quantum theory and postulated the existence of electron orbits within the atom. When electrons occupied these stationary states, no energy was radiated. Bohr moreover ascribed each orbit a certain energy value and this



FIGURE 20 Niels Henrik David Bohr (1885–1962). Photo and permission from Edgar Fahs Smith Collection.

permitted him to derive the formula of Balmer with regard to the spectral lines of the hydrogen spectrum. Bohr published his atomic theory in three voluminous papers, "On the Constitution of Atoms and Molecules," which appeared in the *Philosophical Magazine* between July and November 1913 (Bohr, 1913a,b,c). Although Bohr's theory was primarily of a physical nature, a number of chemical aspects were included as well. He was heavily influenced by the concepts from inorganic chemistry, and he was especially interested in the theoretical explanation of the periodic table (Kragh, 1977). Bohr attempted to explain the various chemical and physical characteristics of the elements by deriving their electronic configurations. This type of approach was not entirely new. As a matter of fact, J. J. Thomson (1856–1940), the discoverer of the electron, had developed the first electronic arrangements in 1904 on the basis of his *plum pudding model* of the atom. Inspired by Victorian vortex chemistry, Thomson had tried to give an explanation of the periodic law, but his attempt had not been very successful (Kragh, 2001). Bohr on the other hand adhered to a *stability condition*, and he selected the least energetic configurations as the most probable ones. Nevertheless, Bohr did not succeed in deriving these configurations deductively from his quantum theories. He was forced to use some inductive reasoning and he had to rely upon his chemical knowledge.

Bohr did not further develop the chemical aspects of his 1913 theory in the subsequent years. He only returned to the subject matter in 1921 when he offered an explanation of the periodic system in terms of electron configurations (Bohr, 1921, 1922a). Bohr referred to the natural system of Mendeleev and Lothar Meyer at the beginning of his Nobel Lecture in Copenhagen in 1922, and he offered his audience a diagrammatic representation of the periodic law in a somewhat modified form of a table first given by Julius Thomsen (Figure 21) (Bohr, 1922b). He noted that the characteristic features of the natural system had found a surprisingly simple interpretation in that the ordinal number of an element in the periodic table, the so-called *atomic number*, is just equal to the number of electrons which move about the nucleus in the neutral atom. He also referred to Moseley's investigations of the X-ray spectra of the elements as convincing support for this law (see Section 5.2).

According to Bohr's opinion, the rare-earth group consisted of elements where the four-quantum level was gradually filled up from 18 to 32 electrons. The number of electrons in the five- and six-quantum levels on the other hand remained unchanged. Bohr's quantum theory thus served as a useful explanation for the pronounced similarity between the chemical and physical properties of the rare-earth elements. He mentioned that their mutual similarity must be ascribed to the fact that we have here to do with the development of an electron group that lies deeper in the atom. He moreover emphasized that lutetium ($Z = 71$) had to be considered the last rare-earth element. Element 72 on the other hand did not belong to

1 H	3 Li	11 Na	19 K	21 Sc	23 V	25 Mn	27 Co	28 Ni	29 Cu	31 Ga	33 As	35 Br	36 Kr	37 Rb	39 Y	41 Nb	43 -	45 Rh	47 Ag	49 In	51 Sb	53 I	55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 -	62 Sm	63 Eu	64 Gd	65 Tb	66 Os	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 -	73 Ta	74 W	75 -	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 -	86 Em	87 -	88 Ra	89 Ac	90 Th	91 Pa	92 U	118 -
2 He	4 Be	12 Mg	20 Ca	22 Ti	24 Cr	26 Fe	28 Ni	30 Zn	32 Ge	34 Se	36 Kr	38 Sr	40 Zr	42 Mo	44 Ru	46 Pd	48 Cd	50 Sn	52 Te	54 Xe	56 Ba	58 Ce	60 Nd	62 Sm	64 Gd	66 Os	68 Er	70 Yb	72 -	74 W	76 Os	78 Pt	80 Hg	82 Pb	84 Po	86 Em	88 Ra	90 Th	92 U	118 -																					

FIGURE 21 Bohr's periodic table (1922). Reproduced with permission (Copyright Nobel Foundation, 1922).

the group of trivalent rare earths, but had to be seen as a tetravalent zirconium homologue. Bohr observed that in many representations of the table a place is left open for this element in the rare-earth family, but he noted that in Julius Thomsen's representation of the natural system, this hypothetical element was given a position homologous to titanium and zirconium (Figure 21).

5.2 Moseley's Research on X-Ray Spectra of Elements

After his graduation as M.A. in Natural Sciences at Trinity College, Oxford, in 1910, Henry Moseley (1887–1915, Figure 22) headed for Manchester where he was welcomed in the laboratory of Rutherford (Hogg, 1975). His measurements of the X-ray emission spectra of the



FIGURE 22 Henry Gwyn Jeffreys Moseley (1887–1915). Photo and permission from Edgar Fahs Smith Collection.

chemical elements rendered the correlation possible between the X-ray frequencies and the atomic numbers of the elements. The main objectives of Moseley's research were to clarify the anomalies in the periodic table and to solve the puzzle of the total number of rare earths (Heimann, 1967). As Moseley observed, "there are some [chemists] who would split almost every one of these rare-earth elements into three or four" (Heimann, 1968). The success of Bohr's theory in the explanation of the hydrogen spectrum undoubtedly led Moseley to speculate on the connection between the frequency, ν , of X-rays and the nuclear charge of the emitting element (Gorin, 1996; Haigh, 1995; Heimann, 1967, 1968; Heimann and Heilbron, 1967; Lesk, 1980). Moseley could thus explain the order of the elements in the periodic table. The reversals of tellurium and iodine, potassium and argon, nickel and cobalt in the periodic system were explained on the basis of their atomic numbers.

Moseley was still working in Rutherford's group in Manchester when he published his first paper on the high frequency spectra of the elements in the issue of the *Philosophical Magazine* for December 1913 (Moseley and Darwin, 1913). Moseley had been investigating the K radiation of at least

10 transition elements from calcium to zinc (with the exception of scandium). At the end of the year, in December 1913, Moseley left the research group of Rutherford and headed for Oxford with the aim of investigating the K spectra of all the other elements, as well as the L spectra of the elements with high atomic weights. The reason for this move to Oxford could be the fact that Moseley was anxious to get full credit for all his research and felt that as long as he stayed in Manchester he was in danger of being overshadowed not only by Rutherford but also by other members of the team which at that time included Geiger, Bohr, Marsden and others (Hogg, 1975). Unfortunately, Moseley's research in Oxford advanced with many difficulties. His X-ray tube had not survived the trip from Manchester to Oxford, and the Clarendon Laboratory in Oxford was in a poor state. Fortunately, Moseley could restart his work soon and he began investigating the K spectra of yttrium, zirconium, niobium, molybdenum, ruthenium, palladium and silver. Elements with an atomic weight greater than $\text{Ag} = 107.8$ could not be studied since the laboratories in Oxford were not built to handle such high voltages.

On January 18, 1914, Moseley enthusiastically wrote to de Hevesy (1885–1966) in Manchester: “[It will] be possible to put every rare-earth element into its right pigeonhole, to settle if any of them are really complex, and where to look for new ones” (Heimann, 1967). His enthusiasm must have faded away however as soon as he moved over to a study of the softer L radiation. The penetrating character of these X-rays was not high enough and the radiation did not pass through the aluminium windows of the spectrometer. Neither did it penetrate through the protective wrapping of the photographic plates. Apparently, two centimeters of air already halted the propagation of the L radiation. His targets moreover volatilized at the high temperatures inside the X-ray tubes. Moseley had to solve these practical problems one at a time. He decided to perform his experiments in the dark and attempted to work with a highly exhausted spectrometer. Since none of the pumps available in Oxford could reach the required high vacuum, Moseley felt obliged to borrow one from the laboratory in Balliol (Hogg, 1975). The L spectra of all the elements from zirconium to gold were subsequently investigated and Moseley observed that the advantage of his method lay in the simplicity of the spectra and the impossibility of one substance making the radiation from another (Heimann, 1968). He thus concluded that his method could even lead to the discovery of missing elements, because of the possibility to predict the position of their characteristic lines.

Soon afterwards, Moseley wrote a second paper on the X-ray spectra of the elements, in which he stated that every element from aluminium to gold (which marked the boundaries of his studies) was characterized by an integer N which determined its X-ray spectrum. This integer N was the atomic number of the element and it was identified with the number of

positive units of electricity contained in the atomic nucleus. Thus, the frequency of any line in the X-ray spectrum is approximately proportional to $A(N - b)^2$, where A and b are constants (Moseley, 1914). The latter statement has been termed *Moseley's law* in his honor (Heimann, 1967). However, the concept of the atomic number was not introduced by Moseley, but by the Dutch amateur scientist Antonius Van den Broek (1870–1926) (Scerri, 2007; Van den Broek, 1913; van Spronsen, 1969). The term “atomic number” was first used by Rutherford (Rutherford, 1913). When the chemical elements were classified on the basis of their atomic number, Moseley immediately observed that elements 43, 61, and 75 were still missing. Moseley's investigations were not only important in establishing the correct order of the elements in the periodic table. They also provided an experimental vindication of the atomic number hypothesis, and therefore increased the explanatory power of the Rutherford–Bohr model (Heimann, 1968). Moseley was killed in the First World War during the battle of the Dardanelles in August, 1915 at the age of 27.

5.3 The Controversial Element 72

At the end of his Noble Lecture to the Swedish Academy of Sciences on December 11, 1922 Niels Bohr announced the discovery of element 72 by George de Hevesy and Dirk Coster (1889–1950) in Copenhagen (Bohr, 1922b). This was a very surprising statement since the French chemist Georges Urbain (1872–1938) had already claimed the discovery of this element in 1911 (Heimann, 1967; Kragh, 1979, 1980, 1996; Scerri, 1994; Urbain, 1911; Weeks, 1956). Urbain had named the element *celtium* and he had recently published some further proof for its existence in collaboration with Alexandre Dauvillier (1892–1979). Urbain was a French chemist and professor of mineral chemistry at the Faculté des Sciences de l'Université de Paris. He was a rare-earth specialist, as well as an amateur composer, painter and sculptor. Urbain became the president of the International Committee on Atomic Weights in 1907 after Henri Moissan (1852–1907) had died, and he must have realized how tactical a position it was during his priority dispute with Auer von Welsbach (1858–1929) (*vide infra*). Urbain improved the current methods of fractionation by selecting a number of more efficient reagents and he was a pioneer in the application of double salts of bismuth during the chemical fractionation of rare earths. This allowed him to disprove Crookes results on radiant matter spectroscopy. Pure rare-earth samples did not show any phosphorescent spectrum, according to Urbain. Urbain was moreover a philosophically inclined scientist and he wrote a number of books on the changing concept of element. In analogy with Crookes' viewpoints, Urbain did not attach great importance to the operational definitions of Lavoisier with regard to the concept of elements, and he also questioned

the trustworthiness of atomic weight determinations in determining the homogeneity of the chemical elements. He therefore proposed to adhere to the magnetic susceptibility of the rare-earth elements as a criterion for their elementarity. Despite the fact that Urbain clearly belonged to the traditional chemists of the nineteenth century and that he approached the rare-earth crisis from a chemical point of view, it appears that he was swift in adopting Moseley's X-ray spectroscopic techniques of analysis. Urbain had initiated his researches in 1907, after having discovered neo-ytterbium (Yb) and lutetium (Lu), and he worked for four years, until he finally obtained a number of new lines in the optical spectrum of one of his fractions and concluded that they had to be attributed to a new element, *celtium* (Ct).

It appears that Moseley had heard about Urbain's discovery and moreover believed in the existence of celtium when he continued his research in Oxford in 1914. Due to a small calculation error, Moseley had ascribed each element from yttrium an atomic number which was one unit too high. For example, yttrium was not allotted the correct atomic number 39, but instead 40. As a consequence, the atomic number 39 remained unused and Moseley wrote to Rutherford on March 4, 1914 that it seemed very probable that N₃₉ would be celtium. Moseley's prediction was in contradiction with Urbain's claim that celtium belonged to the family of rare-earth elements. Moseley soon discovered the flaw in his argument and he redeemed his own mistake the next day on March 5, 1914. He wrote a postcard to Rutherford, claiming that the element between strontium and yttrium was a myth (Heimann, 1967). In his second article of April 1914, Moseley summarized the results of his rare-earth research (Moseley, 1914). He had obtained most rare-earth samples from Crookes and from Schuchard which he subsequently rubbed on the surface of nickel plates (Hogg, 1975). He had begun investigating the spectra of the whole rare-earth family in the middle of February 1914 and ascribed these elements the following atomic numbers:

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
La	Ce	Pr	Nd	–	Sm	Eu	Gd	Tb	Ho	Dy	Er	TmI	TmII	Yb	Lu

Notice that Moseley had made a minor mistake in the atomic number determinations of both holmium and dysprosium. The atomic number of holmium is namely 67, and dysprosium has an atomic number of 66. It also appears that Moseley attached some credence to the investigation of Auer von Welsbach who had demonstrated the complexity of thulium in 1911 by splitting it into three components. Moseley had incorporated two of these components (TmI and TmII) in his atomic number sequence. Moseley therefore ascribed Urbain's neo-ytterbium and lutetium too high an atomic number (in reality the atomic numbers of ytterbium and

lutetium are 70 and 71 respectively). As a consequence, only one case remained vacant (number 61) and Moseley therefore explained to de Hevesy that he was tempted to accommodate celtium in this spot. A few weeks later, Moseley had obtained a number of new samples of ytterbium, lutetium, terbium and dysprosium from Urbain, and he subsequently wrote a second letter to de Hevesy on April 23, 1914, concluding that TmII does not exist, and that he had got the order dysprosium, holmium wrong (Heimann, 1967). Moseley had thus adjusted the sequence of elements and he included the following list in his letter for de Hevesy, with element 61 still missing and celtium having ascribed an atomic number of 72:

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
La	Ce	Pr	Nd	–	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ct

At the end of May 1914, Urbain visited Moseley in Oxford to examine together the X-ray spectrum of celtium. Moseley could not find other lines in the spectra than those of lutetium and ytterbium. Urbain accepted the negative results of Moseley's research, but he did not lose faith in the elementarity of celtium. Urbain started his own X-ray investigations in collaboration with Alexandre Dauvillier in Paris. They announced in May 1922, seven months before Bohr's Nobel Lecture, their discovery of two new X-ray lines which they attributed to celtium on the basis of Moseley's theory, even though the spectrum was very faint and the lines corresponded only roughly with Moseley's predictions.

When Bohr returned from a series of lectures which he had delivered in Göttingen in June 1922, he read a note by Rutherford in *Nature* communicating Urbain and Dauvillier's results. Celtium was considered to be a trivalent rare-earth element. This was in contradiction with Bohr's theory of atomic structure, according to which element 71 was the last rare earth, and element 72 had to be a tetravalent zirconium homologue. But Bohr at first believed he had been wrong, and he accepted Urbain's discovery. Nevertheless, Bohr soon decided to consult with Dirk Coster in Lund (Sweden). Coster was a specialist in X-ray spectroscopy given the fact that he had been the assistant of Manne Siegbahn (1886–1978), the Swedish pioneer in X-ray investigations after Moseley's death. Coster questioned Urbain and Dauvillier's findings, and Siegbahn, who had visited the two Frenchmen in Paris, had not even been able to see the two faint lines on the photographic plates. Bohr asked Coster, when he came to Copenhagen in September 1922, to search for element 72, but Coster was at first reluctant. de Hevesy, however, soon convinced him and the two started their hunt for element 72 in a number of Norwegian zirconium containing minerals which they had obtained from the Mineralogy Museum of Copenhagen. de Hevesy had to perform intensive chemical investigations for almost two weeks, but they finally

succeeded on Saturday, December 9, 1922, to obtain six very pronounced X-ray spectral lines which pointed to the existence of a new element, element 72, according to Moseley's theory. Coster and Kramers decided to name the element *hafnium*, but Bohr, de Hevesy, Bjerrum and Christiansen preferred *danium*. Due to an error of the editor of *Nature*, the element was named *hafnium* after all, in reference to the Latinized name of Copenhagen (*Hafnia*). Their results were published on January 20, 1923.

A first response came from the British chemist and mineralogist at the British Museum, Alexander Scott, who claimed he had discovered element 72 in the period 1913–1918 when analyzing black sand from New Zealand. He had called the element *oceanium*. This finally turned out to be a mixture of iron, aluminium, and titanium. More importantly, a priority dispute between the French school (i.e., Urbain and Dauvillier) and the Copenhagen school (i.e., Bohr, de Hevesy, and Coster) began. It must be noted that while both teams consisted of chemists and physicists, they definitely adhered to different research paradigms: the classic, chemical approach versus the physical, quantum mechanical approach. The French school rested on an enormous chemical knowledge with regard to the rare-earth elements and its members were very skeptical about the theoretical viewpoints of Bohr. Bohr had not soiled his own hands, and he had never personally experienced the troubles of chemical fractionation. How could such a theoretical physicist possibly say anything meaningful about the rare earths? The Copenhagen school on the other hand accepted Bohr's theory of the atom with open arms. They relied upon quantum mechanical viewpoints and were therefore convinced that element 72 would prove to be a zirconium homologue. The Copenhagen school was supported by scientists from Scandinavia, Holland and Germany. The German chemist, Fritz Paneth backed up Coster and de Hevesy in their claims. Auer von Welsbach had lost the priority dispute with Urbain about the elements 70 and 71 and therefore supported the Copenhagen team as well. The French school was mainly supported by French and British scientists. Bohuslav Brauner who had lost the priority dispute with Auer von Welsbach with regard to the splitting of didymium and subsequent discovery of praseodymium and neodymium also supported the team of Urbain. Besides the internal reasons for a priority dispute, there also were a number of external ones. Both nationalistic feelings and personal relations contributed to the whole conflict. The sudden interest from British scientists when Scott had claimed priority over the discovery of element 72 clearly emphasizes the important role of patriotism in priority disputes. The political situation after the First World War also contributed to the conflict between the French and Copenhagen school. French and English scientists were of the opinion that German science formed a threat and they heavily tried to isolate it from the rest of the world.

In February 1923, Urbain and Dauvillier stated in a piercing critique that Coster and de Hevesy had only succeeded in rediscovering the rare-earth element, celtium, in zirconium minerals (Scerri, 1994). Coster and de Hevesy replied by underlining the differences in chemical and physical properties between hafnium and celtium. While the claim of the French scientists rested on two very faint lines in the X-ray spectrum, their claim to the discovery of element 72 rested on six pronounced X-ray lines. Bohr too said he had reason to believe that the observation of Dauvillier was a self illusion. de Hevesy's chemical investigations had moreover proven that hafnium was a tetravalent zirconium analogue, and that it did not behave as a typical, trivalent rare-earth element. They had studied the optical spectrum of hafnium and noticed the enormous differences with Urbain's, 1911 spectra. In the spring of 1923, Urbain and Dauvillier felt obliged to admit that element 72 was a zirconium homologue, but this did not end the dispute. The French team maintained that they had been the first in discovering element 72. Meanwhile, de Hevesy continued his chemical investigations, determining the atomic weight of element 72, as well as the solubility of its salts, mineralogical and magnetic properties. The dispute came to an end when Bohr received some rare-earth samples from Auer von Welsbach, which demonstrated that the optical lines obtained by Urbain were not due to celtium, but were characteristic of lutetium. Urbain's celtium samples of 1911 were just very pure lutetium specimens. They did not contain any new elements. This also meant that his lutetium samples of 1907 had been impure, and did contain only a trace of lutetium. Auer von Welsbach's cassiopeium samples on the other hand had been pure in 1907, and he was to be seen as the real discoverer of element 71 (Paneth, 1923).

5.4 The Elusive Element 61

In 1902, Bohuslav Brauner suspected the existence of an element between neodymium and samarium on the basis of the rather large difference in atomic weights of these two elements, but he could not give experimental evidence for his claim (Brauner, 1902, 1926). In 1913, Moseley had just discovered the atomic numbers of neodymium and samarium to be 60 and 62 respectively (Moseley, 1914; Moseley and Darwin, 1913). Apparently, element 61 was still missing. The quest for this rare-earth element had thus begun (Marinsky, 1996; Trifonov, 1963, 1984; Trifonov and Trifonov, 1982; Weeks, 1956). The physicists had pointed towards the existence of the unknown element and this inspired a number of chemists to start looking for it. Making predictions as to the existence of unknown elements would have been impossible before Moseley's pioneering work. Admittedly, Mendeleev had successfully predicted the existence and

properties of gallium, scandium, and germanium on the basis of his periodic table, but this was due to the fact that these vacant spaces were completely surrounded by known elements. Mendeleev had never been that clear when it came to predicting the properties of eka-caesium (francium), eka-iodine (astatine), dvi-tellurium (polonium), eka-manganese (technetium), dvi-manganese (rhenium), and especially the rare-earth elements.

"I have been searching unsuccessfully for the unknown element," Moseley wrote on April 23, 1914. "Either it is very rare, or as is quite likely, only occurs in a few minerals. I hardly think that it does not exist" (Heimann, 1967). Most chemists however were quite surprised by Moseley's prediction. It was known since the 1920s that the rare-earth elements were not rare at all. Their abundance in the earth's crust was greater than those of tin, lead, silver, antimony, mercury, and gold. The family of rare earths was moreover subdivided into two groups. The cerium group contained all rare-earth elements with low atomic weights. The yttrium group on the other hand was constituted of rare earths with high atomic weights. Both chemists and geologists knew that the members from the cerium group were more abundant than those of the yttrium group. Moseley's investigations, on the other hand, demonstrated that all members of the yttrium group were known. Strangely enough, the unknown element appeared to belong to the cerium group. Clearly, the mysterious element 61 was completely different from the other cerium group elements. Its abundance had in all probability been too low in order to render its discovery possible with the aid of the current methods of analysis (Yntema, 1924). However, in April 1926 an article appeared in *Nature* from the hand of the American chemists James Allen Harris, Leonard Yntema, and B. Smith Hopkins from the University of Illinois at Urbana-Campaign, who claimed to have discovered element 61 in natural minerals (Harris et al., 1926a,b). They named the element *illinium* (Il). Apparently, Yntema had performed thousands of fractional crystallization, after which all the neodymium and samarium containing fractions had been investigated by Harris and Hopkins with the aid of optical spectroscopy and X-ray spectroscopy. But despite the fact that their spectroscopic results pointed towards the presence of element 61, the team of American scientists had not yet succeeded in isolating illinium. It must also be noted that at that time all chemical elements had been discovered by European scientists. The past "element" discoveries of American chemists had all proved to be erroneous. This made the discovery of element 61 all the more important.

However, shortly after this announcement two Italian chemists, Luigi Rolla (1882–1960) and Lorenzo Fernandes (1902–1977), who were working at the University of Florence, claimed to have discovered element 61 in monazite from Brazil two years before the Americans, back in 1924 (Rolla and Fernandes, 1926, 1927a,b,c, 1928). All their results had been meticulously written down in two long papers, but they had decided not to

publish it for some obscure reasons. The articles were instead filed away in a sealed envelope and subsequently placed in safekeeping in the *Accademia dei Lincei* in Rome. Not surprisingly, a priority dispute commenced between the Americans and the Italians. Everyone wondered who had been the true discover of element 61 and whether one should call it illinium or rather *florentium*, as the Italians preferred? Two German chemists, the rare-earth specialist Wilhelm Prandtl (1878–1956) and his assistant Hans Grimm had investigated more than 50 different rare-earth minerals with the aid of X-ray spectroscopy, but they could not retrace the element 61 (Prandtl, 1926; Prandtl and Grimm, 1924, 1926). They concluded that the element 61 differed from the rare-earth metals in its chemical behavior or that it does not exist at all. They had constructed a periodic table and noticed that the elements 43, 61, 75, and 93 in the periodic table were all located underneath each other in the manganese group VIIb. They stated that the empty slots 43, 61, 75, and 93 could be a manifestation of some periodic regularity and that it was possible that they would never be filled.

Auer von Welsbach was another chemist who doubted the validity of the American results. Finally, the married couple, Ida Noddack (née Tacke, 1896–1978) and Walter Noddack (1893–1960), embarked upon a quest for the element 61. Husband and wife were greatly stimulated by their recent discoveries of masurium and rhenium. The Noddacks, in collaboration with Berg, began their investigations with an enormous amount of rare-earth minerals (Noddack et al., 1925). They first of all produced a number of very pure samples of neodymium and samarium. They made use of the most sensitive and accurate methods of analysis of that time, allowing to detect element 61 if it were 10 million times more rare than neodymium and samarium. However, their work remained without success.

Ida Noddack suspected that element 61 was radioactive and presumed its half-life to be less than the age of the earth. The geochemists on the other hand could not believe such a statement. In view of the fact that all the members of the cerium group were both abundant and stable, they were quite certain about the possibility of finding element 61 in nature. They had also observed that the rare-earth elements did not always exhibit a valency of three, and that some rare earths possessed a valency value of two or four. Europium, for example, formed stable compounds when its oxidation state was +II. Perhaps, something similar could be observed with element 61. Maybe all chemists had just been looking for this element in the wrong place. Instead of analyzing rare-earth minerals, why not looking in minerals containing bivalent alkaline earths? The Noddacks did not attach much credence to this viewpoint, but they nevertheless pursued their research in the latter type of minerals. Unfortunately, all appeared to be in vain.

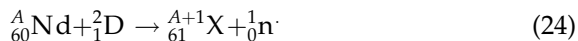
It was the German theoretical physicist, Josef Mattauch (1895–1976), who proved Ida Noddack to be correct, when he proposed the *Mattauch rule* (also

known as the *Mattauch isobar rule*) (Mattauch, 1934). According to this rule, if the nuclear charges of two isobars (i.e., nuclides with the same mass number) differ by unity, one of the isobars must be radioactive. Another formulation of this rule is that if two adjacent elements have nuclides of the same mass, then at least one of them must be radioactive. Isobars can only be stable when they are separated by more than one atomic mass unit. The mass numbers of the stable isotopes of neodymium and samarium are:

Nd	142	143	144	145	146	–	148	–	150
Sm	–	–	144	–	–	147	148	149	150

All the possible mass numbers between 142 and 150 are already taken by neodymium ($Z = 60$) and samarium ($Z = 62$), so that no stable isotope is expected for element 61. They would all be radioactive, just as in the case of technetium ($Z = 43$). The Mattauch rule however was not capable of ascribing these radioactive isotopes a certain half-life. A number of uranium and thorium isotopes are also radioactive, but their half-lives are great enough so that one can still find them in nature. During that same year, in 1934, the American physicist and future Noble Prize winner, Willard Libby (1908–1980), discovered that neodymium is a β emitter (Libby, 1934). According to Soddy's displacement laws, this should imply that when neodymium decays, isotopes of element 61 should be formed.

Due to these recent discoveries, chemists did not lose their faith and they still hoped to discover the element 61 in nature. But most of them realized that it would probably be more successful to synthesize the element artificially. Technetium, the first artificially prepared element, had been formed in 1937 in the Berkeley cyclotron (Perrier and Sègre, 1937, 1947). One year later, in July 1938, the American physicists Pool and Quill of the University of Ohio started bombarding a neodymium target with fast deuterons (Pool and Quill, 1938). They were hoping that the proton would be taken up by the neodymium nuclei, with the formation of element 61 as a consequence:



Unfortunately, the produced amount of element 61 was too small to study its properties. Pool and Quill were nevertheless convinced that they had synthesized an isotope of element 61 with mass number 144 and half-life of 12.5 h. More isotopes of element 61, with mass number 144, 147, and 149, were produced two years later in collaboration with Kurbatov, Law and MacDonald (Kurbatov et al., 1942; Law et al., 1941). Pool and his team decided to name the element *cyclonium* (symbol: Cy) in honor of the cyclotron in which all artificial elements had been formed. Most chemists however questioned the validity of their assertions, and doubted that the neodymium targets had been entirely pure. Every presence of impurities

would have been bombarded too and these could have formed some rare-earth isotopes.

In the year 1932, the *neutron* was discovered by Sir James Chadwick (1891–1974) as a new, neutral elementary particle which constituted the atomic nucleus (Chadwick, 1932). Since it was not electrically charged, it proved very useful to penetrate the nuclei of other atoms in order to form new nuclides. Physicists soon discovered the processes of fission when they started bombarding certain uranium isotopes with neutrons. They produced daughter nuclides ranging from zinc to gadolinium. It thus appeared that isotopes of the element 61 could be produced during the fission process of uranium-235 as well. A number of chemists, physicists, and engineers studied the formation of these isotopes during the Manhattan Project in 1942. A whole range of new techniques had to be developed in order to separate the different nuclides. The ion exchange chromatographic methods proved very valuable. Polymers were used as ion exchangers. The American chemists Jacob Akiba Marinsky (1918–2005), Lawrence Elgin Glendenin (1918–2008) and Charles Dubois Coryell (1912–1971) working at Oak Ridge National Laboratory (ORNL) in Tennessee soon succeeded in separating the different lanthanide nuclides. They also obtained some fractions which contained element number 61. In 1945, a millionth of a gram was obtained of the isotopes with mass number 147 and 149. These isotopes had been generated by two different methods: nuclear fission of uranium and bombardment of neodymium with neutrons. Finding a name for element 61 proved however as difficult as the production of its isotopes. It was Coryell's wife Grace Mary who proposed to name the element *promethium* (symbol: Pm). The mythical Prometheus, one of the titans in Greek mythology, had stolen the fire from the gods for the benefit of mankind. Zeus decided to punish Prometheus for his acts and he chained him to a big rock. An eagle came to visit him each day and always ate a small piece of his liver, just small enough so that it could grow again in one day. The choice of their name was twofold. For one thing, it referred to the harnessing of nuclear energy by humans in order to synthesize new elements. On the other hand, the name warned everybody for the "eagle of war." The discovery of promethium was first announced at an American Chemical Society Meeting in New York in September 1947 (Marinsky et al., 1947). On July 28, 1948, a total of 3 mg of yellow promethium chloride and pink promethium nitrate were exhibited before the American Chemical Society.

5.5 Intergroup Accommodation Methodologies

According to the *intergroup accommodation methodology*, the rare-earth elements did not show any relationship with the other elements. They had to be placed within the periodic table as a separate family of elements,

completely unconnected to the other groups. This was accomplished by accommodating the rare earths in between two groups of the periodic table. The rare-earth elements thus showed some analogy with the transition metals in view of the fact that both types of elements were separated from the rest of the system and that both formed in a sense the transition between two main groups of Mendeleev's system. This type of placement was in complete agreement with Bohr's quantum theory of the atom, and consequently became the preferred methodology in the twentieth century.

A particularly interesting classification was the one with horizontal groups and vertical periods proposed by the Danish thermochemist Hans Peter Jørgen Julius Thomsen (1826–1909) in 1895 (Figure 23) (Thomsen, 1895). Such a pyramidal/ladder form representation had already been proposed by the English scientist Thomas Bayley in 1882 (Figure 24), but

Elektropositive Elemente.

				Cs 133
				Ba 137
				La 138
				Ce 140
				Ne 141
				Pr 144
				— —
				Sm 150
				— —
				Gd 156
				Trb 160
				— —
				Er 166
				— —
				Thu 171
				Yb 173
				— —
				— —
				Ta 183
				W 184
				— —
				Os 191
				Ir 193
				Pt 195
				Au 197
				Hg 200
				Tl 204
				Pb 207
				Bi 209
				— —
				— —

Elektronegative Elemente.

FIGURE 23 Julius Thomsen's pyramidal periodic table (1895). Reproduced from Thomsen (1895).

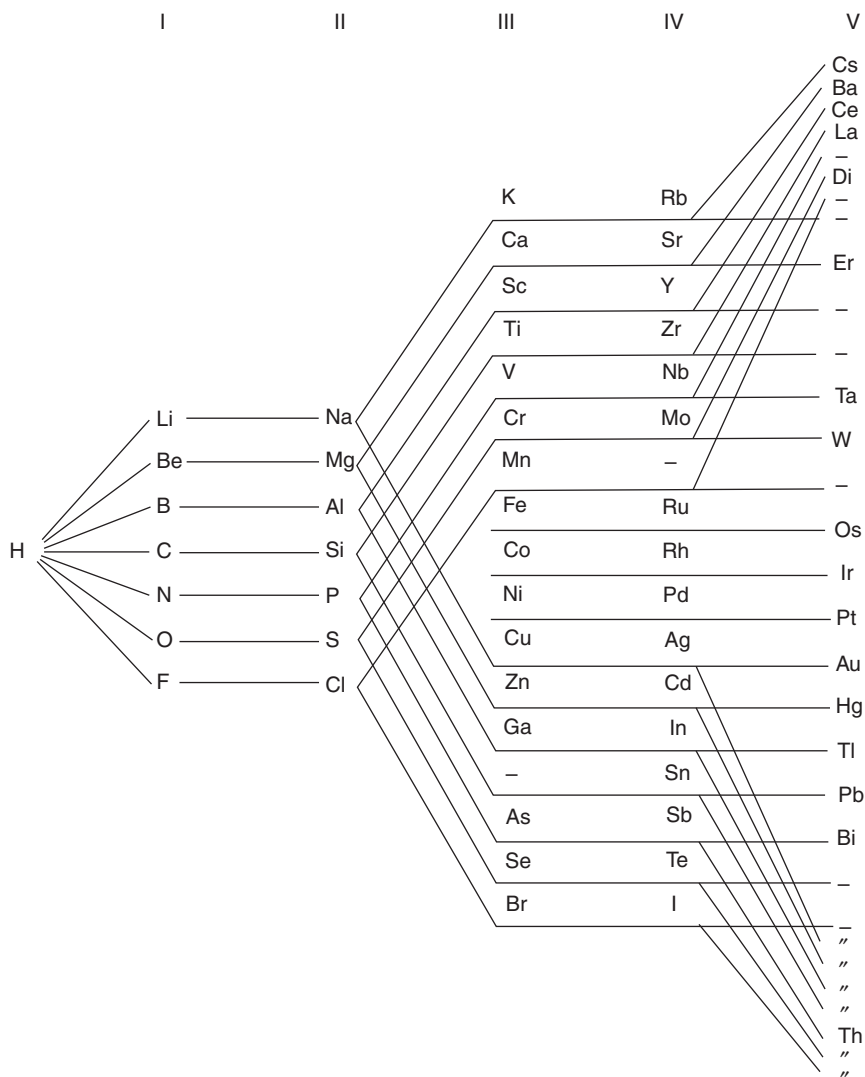


FIGURE 24 Bayley's pyramidal periodic table (1882). Reproduced from [Bayley \(1882\)](#).

Thomsen's system differed from Bayley's pyramid in an important way. Both tables consisted of three main parts. The first part contained the elements of the short periods (Li–F and Na–Cl); the second part included the long periods of 17 elements (K–Br and Rb–I); and the third section covered the remaining 31 elements from cesium to uranium. Analogous elements were connected by lines and due to the existence of odd and even series, most elements were related to a pair of elements. Thus Na was related

with K and Cu (and therefore also with Rb and Ag). Some elements remained completely unconnected. These were the transition metal triads {Fe, Co, Ni}, {Ru, Rh, Pd}, and {Os, Ir, Pt} which represented a transition from the odd to the even series. The important difference between the two tables is that Thomsen connected the elements Rb–Ag with only one element, instead of two as Bayley did. The consequences were explained by Thomsen in his paper:

Just as silicon in the first group shows similarities with titanium on the one hand and with germanium on the other, there exists in exactly the same way a relationship between the elements of the 2nd and 3rd groups, for example from zirconium to cerium with an atomic weight of 140 on the one hand and from zirconium to an unknown element with an atomic weight around 181 on the other. There are a large number of rare-earth elements in between these two elements which are related to one another like the central elements of the 3rd series placed between manganese and zinc. (Thomsen, 1895; Trifonov, 1966).

Thomsen even tried to explain the analogy between the rare-earth elements on the one hand and the elements from group VIII on the other, just as Mendeleev had tried 26 year earlier (see [Section 3](#)). But the most important aspect of Thomsen's table was not the apparent analogy with the transition metals, but the fact that the rare-earth elements did not bear any relationship with the elements of the preceding period from Rb to I (except for La, Ce and Yb). The rare earths did not belong to any of the eight groups and they were fitted in between group IV and V as an intergroup. Thomsen moreover correctly predicted the existence of a total of 15 rare earths from lanthanum to the unknown element after ytterbium. The element with atomic weight 181 did not belong to the rare-earth elements, but was a zirconium homologue. One thus starts to understand why Bohr preferred this table and why he used it during his Noble Lecture in 1922 ([Figure 21](#)) ([Bohr, 1922b](#)). The element after ytterbium was lutetium, a genuine trivalent rare earth, while element 72 clearly was a tetravalent zirconium homologue. Bohr remembered this table from his student time. A large version of Thomsen's table hung in one of the auditoria of the Polytechnical Institute where Bohr was following the lectures on inorganic chemistry from Niels Bjerrum (1879–1958).

The sequence of rare earths in Thomsen's table was almost correct. He left a number of vacant spaces between Pr and Sm for element 61 (Pm), between Sm and Gd for Eu, between Tb and Er and between Er and Tm for Dy/Ho, and after Yb for Lu and Hf. Bohr was not the first to grasp the advantages of Thomsen's intergroup layout. Both [Richards \(1898\)](#) and the Australian chemist [Steele \(1901\)](#) adhered to the intergroup methodology. It must also be noted that Thomsen's system was not the first so-called

inverted system, with horizontal groups and vertical periods. The chemist Henry Bassett (1892) had proposed a similar system and he also adhered to the intergroup methodology (Figure 25). The rare-earth elements thus formed a separate group and consisted of 18 elements. If these systems would be reverted again, vertical groups and horizontal periods would be obtained.

Alfred Werner (1866–1919) was the first to publish a long form table according to the intergroup methodology (Figure 26) (Werner, 1905a,b). The rare-earth elements (La–Yb) were isolated from the other elements and formed an intergroup between group II and group III. Lanthanum did not belong to the same group as scandium and yttrium. Lutetium on

					Cs 133	226?			
					Ba 137	?			
					La 138·2	?			
					Ce 140·2	Th 232·6			
					Ndy 140·8	?			
					Pdy 143·6	U 239·6			
					148?	241?			
					Sm 150	?			
					?	?			
					?	?			
					154?	248?			
					?	?			
					Tb 159·5	?			
					Ho 162	?			
					?	?			
					Er 166·3	?			
					169?	263?			
					Tm 170·4				
					?				
					Yb 173				
					K 39·1	Rb 85·5	174?		
					Ca 40	Sr 87·6	?		
					Sc 44	Y 89·1	?		
					Ti 48	Zr 90·6	?		
					V 51·4	Nb 94	Ta 182·6		
					Cr 52·1	Mo 96	W 184		
					Mn 55	100?	189?		
					Fe 56	Ru 101·6	Os 191·7		
					Ni 58·7	Rh 103·5	Ir 193·1		
					Co 59	Pd 106·6	Pt 195		
					Li 7	Na 23	Cu 63·4	Ag 107·9	Au 197·3
					Be 9	Mg 24·3	Zn 65·3	Cd 112	Hg 200
					B 11	Al 27	Ga 69	In 113·7	Tl 204·2
					C 12	Si 28·4	Ge 72·3	Sn 119	Pb 207
					N 14	P 31	As 75	Sb 120	Bi 208·9
					O 16	S 32·1	Se 79	Te 125	?
					F 19	Cl 35·5	Br 80	I 126·9	216?

FIGURE 25 Bassett's periodic table (1892). Reproduced from Bassett (1892).

																		He	
																		4	
H																		Ne	
1,008																		20	
Li																		Be	
7,03																		9,1	
																		B	
																		12	
																		C	
																		14,04	
																		16,00	
																		19	
																		20	
Na																		Mg	
23,05																		24,36	
																		Al	
																		27,1	
																		Si	
																		28,4	
																		P	
																		31,0	
																		S	
																		32,06	
																		Cl	
																		35,45	
																		A	
																		39,9	
K																		Ca	
39,10																		40,1	
																		Sc	
																		44,1	
																		Ti	
																		48,1	
																		V	
																		51,2	
																		Cr	
																		52,1	
																		Mn	
																		55,0	
																		Fe	
																		55,9	
																		Co	
																		58,9	
																		Ni	
																		58,7	
																		Cu	
																		63,6	
																		Zn	
																		65,4	
																		Ga	
																		70	
																		Ge	
																		72	
																		As	
																		75,0	
																		Se	
																		79,1	
																		Br	
																		79,96	
																		Kr	
																		81,12	
Rb																		Sr	
85,4																		87,6	
																		Y	
																		89,0	
																		Zr	
																		90,7	
																		Nb	
																		94	
																		Mo	
																		96,0	
																		Ru	
																		101,7	
																		Rh	
																		103,0	
																		Pd	
																		106	
																		Ag	
																		107,83	
																		Cd	
																		112,4	
																		In	
																		114	
																		Sn	
																		118,5	
																		Sb	
																		120	
																		Te	
																		127,6	
																		I	
																		126,9	
																		Xe	
																		131,3	
Cs																		Ba	
133																		137,4	
																		La	
																		139	
																		Ce	
																		140	
																		Nd	
																		145,5	
																		Pr	
																		140,9	
																		Sm	
																		160,3	
																		Eu	
																		151,7	
																		Gd	
																		158	
																		Tb	
																		160	
																		Ho	
																		162	
																		Er	
																		166	
																		Tm	
																		171	
																		Yb	
																		173,0	
																		Ta	
																		182	
																		W	
																		184,0	
																		Os	
																		191	
																		Ir	
																		193,0	
																		Pt	
																		195,1	
																		Au	
																		197,2	
																		Hg	
																		200,6	
																		Tl	
																		204,1	
																		Pb	
																		207,2	
																		Bi	
																		209,0	
																		Po	
																		209	
																		At	
																		210	
																		Rn	
																		222	
Ra																		Ac	
226																		227	
																		La	
																		139	
																		Ce	
																		140	
																		Th	
																		232,0	
																		U	
																		238,1	

FIGURE 26 Werner's periodic table with an intergroup accommodation of the rare-earth elements (1905). Reproduced from [Werner \(1905b\)](#).

the other hand, according to Werner's table, was not a rare-earth element, but a transition metal (see also Section 7). Werner was moreover the first to suggest the existence of another intergroup of heavier elements, below and analogous to the rare-earth elements. This idea was taken up by Glenn Seaborg and is now known as the *actinide hypothesis* (see also Section 6). In Werner's system, the pair praseodymium–neodymium has been arranged according to decreasing atomic weight: Werner placed neodymium (143.6) before praseodymium (140.5). The reason given by Werner for this proposal was the similarity in color of the hydrated cobalt (II) and neodymium(III) salts which are violet on the one hand, and the similarity in color of the hydrated nickel(II) and praseodymium(III) salts which are green on the other hand. The order cobalt–nickel in the periodic table suggested Werner to choose the order neodymium–praseodymium as well. Notice that the pair cobalt–nickel is an example of the deviation from increasing atomic weight in the periodic table. Baur (1911) published a similar table, but he included the rare earths between group IV and V (except La and Ce, see Figure 27). The best representation, according to the authors' opinion, was the *left-step periodic table* which had been devised in the period 1927–1929 by the French engineer, inventor and biologist Charles Janet (1849–1932) (see Section 7). A remarkable periodic system is the circular system of Janet (Janet, 1929), which was based on his left-step table (Figure 28). The advantage of this representation is its compactness. Janet's table gives equal value to all the elements, including

Nullte Gruppe	Erste Gruppe		Zweite Gruppe		Dritte Gruppe		Vierte Gruppe		Gruppe der seltenen Erden	Fünfte Gruppe		Sechste Gruppe		Siebente Gruppe	Eisen-Platin-Gruppe
	Haupt- gruppe	Neben- gruppe	Haupt- gruppe	Neben- gruppe	Haupt- gruppe	Neben- gruppe	Haupt- gruppe	Neben- gruppe		Haupt- gruppe	Neben- gruppe	Haupt- gruppe	Neben- gruppe		
He	Li	Be	B	[C					N	O	F				
Ne	Na	Mg	Al] Si					P	S	Cl				
Ar	K	Ca	Sc	Ti						V	Cr				Mn Ni Fe Co
		Ca	Zn	Ga	Ge				[As	Se	Br				
Kr	Rb	Sr	Y	Zr						Nb	Mo				Ru Rh Pd
		Ag	Cd	In	Sn				[Sb	Te	J				
X	Cs	Ba	La	Ce					{Pr Sm Gd Dy Er Yb Nd Eu Tb Ho Tu Lu	Ta	W				Os Ir Pt
		Au	Hg	Tl	Pb					[Bi	Pol.			Supra- jod	
Em	Supra- cäs.	Ra	Akt.	Th						Supra- tantal	U				

FIGURE 27 Baur's periodic table (1911). Reproduced from Baur (1911).

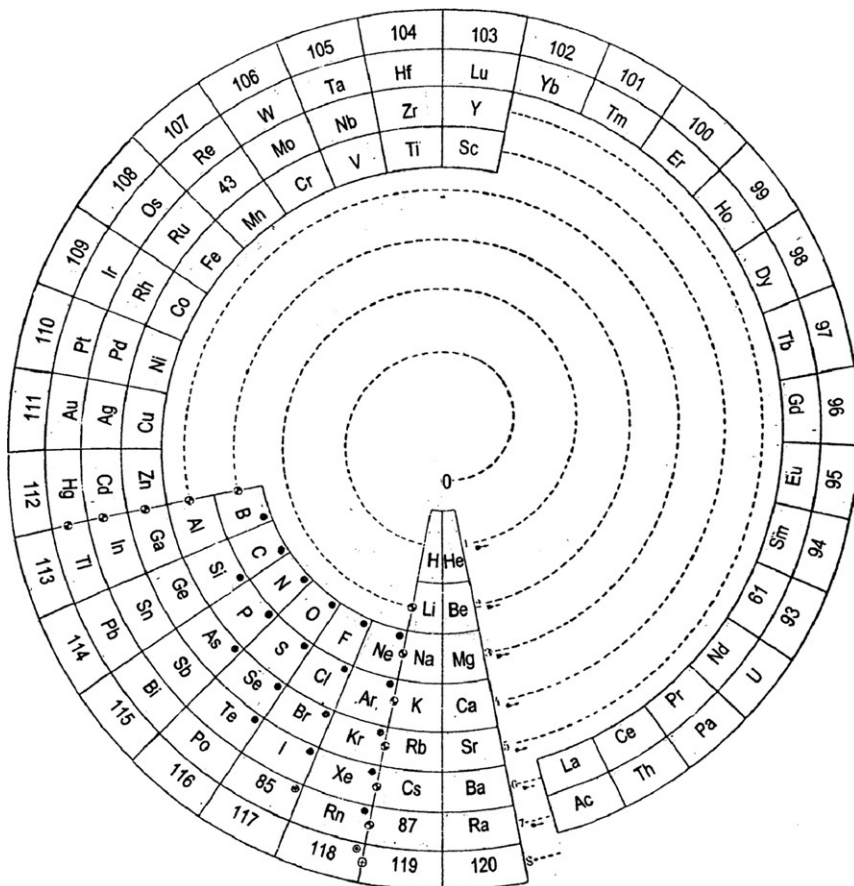


FIGURE 28 Modified circular system of Janet (1929). Reproduced from Stewart (2007), with permission of Springer.

the rare earths. Notice that Janet places lutetium and not lanthanum below yttrium (see Section 7).

A survey of about 100 educational and professional textbooks in the field of descriptive inorganic chemistry was entailed by one of the authors (P.T.) in order to investigate the popularity of the three types of accommodation. A total of 92 chemistry textbooks for both undergraduate and graduate students from the period 1846–1963 was selected at random and thoroughly investigated. Only 54 manuals out of the 92 did contain a periodic table. One handbook exhibited a spiral form of the periodic table (Shepard, 1886), but all other textbooks represented short and long forms of the periodic table. An important observation rested on the fact that almost all textbooks adhered to one of two possible accommodation

methodologies. Thus 40 textbooks placed the rare-earth elements according to a homologous accommodation, and the other 14 adhered to the intraperiodic accommodation methodology. The first intergroup accommodation only appeared in 1946 (Yost and Russell, 1946). Indeed, the well known placement of both lanthanides and actinides underneath the main body of the “modern” periodic table became only popular after the Second World War.

6. SEABORG'S ACTINIDE CONCEPT

Although Bohr considered thorium, protactinium, and uranium as members of a second series of rare earths, the majority of chemists remained convinced that these elements were homologues of hafnium, tantalum and tungsten, for a time after Bohr had formulated his atomic theory. The reason for the delay of acceptance of a second rare-earth series was mainly due the fact that the highest valence states of thorium (+IV), protactinium (+V) and uranium (+VI) suggested that these elements were transition metals. Moreover, with the exception of thorium and cerium, there are, besides the similarities in electronic configuration, only few similarities in chemical properties between the early actinide elements and the lanthanides. The chemical properties of uranium seem to differ very much from those of neodymium, whereas on the other hand there are striking similarities between uranium and the elements of group 5 (Cr, Mo, W). For instance, uranium and tungsten both form hexachlorides (UCl_6 and WCl_6). Uranium forms the ion $\text{U}_2\text{O}_7^{2-}$ and the compound UO_2Cl_2 , while chromium forms $\text{Cr}_2\text{O}_7^{2-}$ and CrO_2Cl_2 . However, one should note that the dissimilarities between uranium and neodymium are only evident when hexavalent uranium (the most common oxidation state for uranium) and trivalent neodymium (the most common oxidation state for neodymium) are compared. Uranium(III) on one hand, shows many similarities with neodymium(III), whereas on the other hand, uranium(IV) resembles thorium(IV) and cerium(IV). Another point of confusion was the very small energy differences between the 5f- and 6d-shell, even in the range of the chemical binding energy, so that it was difficult to predict when the 5f-shell started to be filled. It was assumed that in thorium, protactinium, and uranium the 6d-shell was being filled. Goldschmidt (1924) predicted that the transuranium elements up to element 96 would be platinum group elements. Nevertheless, several researchers believed in the existence of a second series of rare earths, even before the introduction of Bohr's atomic theory in 1922. As early as 1892, Bassett considered thorium and uranium to be analogous to cerium and praseodymium, respectively (Bassett, 1892). It should be noted that he preferred the order {Ce, Nd, Pr} rather than {Ce, Pr, Nd} for the

lanthanides. Werner considered thorium as an analogue of cerium and uranium as an analogue of europium. Both authors reserved open spaces in their periodic tables for other members of the second rare earths series that were still undiscovered at that time.

In 1926, Goldschmidt demonstrated the analogies between the elements {Th, Pa, U} and the lanthanides on the basis of the observation that the volumes of Th^{4+} and U^{4+} showed the same contractions as the ions of the lanthanide series. Striking early examples of periodic tables in which actinium, thorium, protactinium, and uranium are considered as homologues of the rare earths lanthanum, cerium, praseodymium, and neodymium are the circular system and left-step table of Charles Janet (Janet, 1929).

Seaborg (1944, 1945) noticed that whereas thorium, protactinium, and uranium showed similarities in chemical behavior with zirconium, tantalum, and tungsten, respectively, neptunium and plutonium did not show such similarities with rhenium and osmium, or with technetium and ruthenium. For instance, in contrast to the volatiles osmium tetroxide and ruthenium tetroxide, there exists no volatile plutonium tetroxide. On the other hand, the chemical properties of neptunium and plutonium are very similar to those of thorium and uranium. These four elements have a stable +IV oxidation state. ThO_2 , UO_2 , NpO_2 , and PuO_2 are isomorphous and there is a steady decrease of the metallic ion radius when going from Th^{4+} to Pu^{4+} . Other evidence was based on magnetic susceptibility data, on the absorption spectra of the ions in aqueous solution and in crystals, on the spectra of the gaseous atoms, and on additional crystallographic and chemical data. These observations made Seaborg propose the existence of a second rare-earth series that begins with actinium, in the same sense as that the lanthanide series begins with lanthanum. He termed this second rare-earth series the "*actinide series*." The actinide elements do not tend to occupy the 6d orbital, but there is a gradual filling of the 5f shell over the actinide series. Although Seaborg assumed that thorium would be the first element at which the 5f orbital becomes occupied, he also considered the possibility that thorium and protactinium do not have 5f electrons, and that uranium has three 5f electrons. The actinide concept has as a consequence that +III is a characteristic oxidation state for the actinides. However, a striking difference between the lanthanide and actinide series is the existence of oxidation states higher than +IV in the actinide series (+V and +VI). This is an indication that the 5f electrons are less tightly bonded than the 4f electrons. Seaborg (1949) introduced the form of the periodic table with which so many chemists are familiar with: one that considers the lanthanides and actinides as footnotes of the main body of the periodic table. A detailed account of the development of the actinide concept can be found in Chapter 118 in this Handbook (Seaborg, 1994).

	1 IA																		18 0
1	H	2 IIA												13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	He
2	Li	Be												B	C	N	O	F	Ne
3	Na	Mg	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIIB	10 ---	11 IB	12 IIB		Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn							

6	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
7	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

14CeTh medium-long form periodic table

	1 IA																		18 0
1	H	2 IIA																	He
2	Li	Be												B	C	N	O	F	Ne
3	Na	Mg	3 IIIB																
4	K	Ca	Sc											Al	Si	P	S	Cl	Ar
5	Rb	Sr	Y											In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
7	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

s-block d f-block d-block p-block

14CeTh long form periodic table

FIGURE 30 A medium-long form and long form depiction of the 14CeTh periodic table. In this representation, the f-block consists of 14 groups of f-elements with cerium (Ce) and thorium (Th) as the first representatives of each row and lutetium (Lu) and lawrencium (Lr) as the last ones. Lanthanum (La) and actinium (Ac) are accommodated as d-block elements in group 3 (IIIB) of the periodic table, below scandium (Sc) and yttrium (Y). The d-block has been torn apart in the long form, due to the insertion of the f-block.

of f-block elements to 28 (i.e., 2×14), but there exist two different opinions. The first group of chemists adheres to the 14CeTh tables (Figure 30) and they consider Ce and Th to be the first representatives of the lanthanides and actinides respectively, while Lu and Lr form the other boundary. The second group of chemists, on the other hand, shifts the boundary one box to the left and they look upon La and Ac as the first representatives of the f-block elements, and Yb and No as the last ones. This type of accommodation is represented in the 14LaAc tables (Figure 31). In the 15LaAc table, it seems that the two boxes below scandium (Sc) and yttrium (Y) in group IIIB (group 3) remain vacant, but as Jensen (2008b) correctly pointed out, they rather contain the symbols La–Lu and Ac–Lr, respectively, thus indicating that all these 30 elements in the footnote belong in just those two boxes. This becomes clear when expanding the medium-long form into the long form. However, this interpretation does not go back to the electronic interpretations of the 1920s, as Jensen stated, but to Bohuslav Brauner's asteroid hypothesis of 1902, in which the entire group

	1																		18
	1A	2																	0
1	H	He																	
2	Li	Be																	
3	Na	Mg	3	4	5	6	7	8	9	10	11	12							
			IIIB	IVB	VB	VIB	VII B	VIII B	IX B	X B	XI B	XII B							
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn							

6	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
7	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

14LaAc medium-long form periodic table

	1																		18
	1A	2																	0
1	H	He																	
2	Li	Be																	
3	Na	Mg																	
4	K	Ca																	
5	Rb	Sr																	
6	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb			
7	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No			

s-block f-block d-block p-block

14LaAc long form periodic table

FIGURE 31 A medium-long form and long form depiction of the 14LaAc periodic table. In this representation, the f-block consists of 14 groups of f-elements with lanthanum (La) and actinium (Ac) as the first representatives of each row and ytterbium (Yb) and nobelium (No) as the last ones. Lutetium (Lu) and lawrencium (Lr) are accommodated as d-block elements in group 3 (IIIB) of the periodic table, below scandium (Sc) and yttrium (Y). The 14LaAc periodic table is in perfect agreement with the Madelung rule.

of rare earths should occupy a single place in the system which ordinarily would belong to a single element (Section 4.3). Admittedly, this is the only representation where the similarity of the lanthanide elements is rendered clear. Nevertheless, one cannot agree with this type of accommodation because the whole f-block gets included into the d-block, and no intermingling of the s-, p-, d-, and f-blocks is allowed in the modern periodic table. As a consequence, the discussion gets shifted from where the lanthanides and actinides should be placed as a whole to which two elements should come underneath scandium (Sc) and yttrium (Y) in the third group (IIIB). This could be either lanthanum (La) and actinium (Ac) as depicted in the 14CeTh table, or lutetium (Lu) and lawrencium (Lr) as in the 14LaAc table. When taking the 14CeTh table into consideration, one notices that the d-block has been torn apart due to the insertion of the f-block. Of course, the d-block could be restored by merging the two parts together, but this would result in a non-logical table where the natural sequence of atomic numbers gets interrupted twice, as depicted in Scerri's letter (Scerri,

2009a). In the 14LaAc table, on the other hand, the d-block has remained intact. Thus, from just having a quick look at both tables, one has to admit that the 14LaAc table looks more “natural.” This intuitive thesis can be moreover scientifically substantiated.

There is quite a lot of chemical evidence that lutetium, instead of lanthanum, should be placed in the same column of the periodic table as scandium and yttrium. This issue has been addressed by several authors (Dash, 1967; Hamilton, 1965; Hamilton and Jensen, 1963; Jensen, 2009; Laing, 2005; Lavelle, 2008a; Merz and Ulmer, 1967; Nuroh and Wendin, 1981; Sanderson, 1964; Scerri, 2009a; Villar, 1966) and in a very convincing way by Jensen (1982). Even simple physical and structural properties of the elements are in favor of placing lutetium and not lanthanum below yttrium in the periodic table. The melting point of La is 918 °C, while those of Sc, Y, and Lu are 1,541 °C, 1,522 °C, and 1,663 °C, respectively (Beaudry and Gschneidner, 1978). The room-temperature crystal structure of Sc, Y, and Lu is the hexagonal closed packed (hcp) structure, whereas La has a different hexagonal structure, which is also found for the lanthanides and for the transuranium elements. Sc₂O₃, Y₂O₃, and Lu₂O₃ have the same crystal structure, but the crystal structure of La₂O₃ is different. Also ScCl₃, YCl₃ and LuCl₃ belong to the same structural type, but LaCl₃ does not. X-ray spectroscopy has shown that lutetium, but not lanthanum, has a structure of its conduction band that is similar to that of transition metals (Nuroh and Wendin, 1981). Scandium, yttrium and lutetium are not superconductive at atmospheric pressure, but lanthanum metal becomes conducting at 4.9 K (Probst and Wittig, 1978). Also trends in the atomic radii, the sum of the first two ionization potentials, and the electronegativity favor the grouping (Sc, Y, Lu) instead of (Sc, Y, La). Lanthanum occurs together with the cerium group elements in minerals, whereas lutetium and yttrium occur together with the other yttrium group elements.

With so much chemical and physical evidence supporting the accommodation of lutetium below yttrium in the periodic system, one can wonder why in so many periodic tables lanthanum is placed below yttrium. The answer lies according to Jensen (1982) in incorrect older electronic configurations. The accommodation of the elements in the periodic table is based on electronic configurations and the concept of the differentiating electron. Earlier spectroscopic work seemed to indicate that, with a few exceptions, the ground state electronic configuration of the rare earth atoms was of the form [Noble Gas]($n - 2$)f ^{$x-1$} ($n - 1$)d¹ns². Ytterbium was assigned the ground state [Xe]4f¹³5d¹6s² and lutetium the ground state [Xe]4f¹⁴5d¹6s². These two ground state configurations differ only in the number of electrons in the 4f orbitals. Lutetium has a 4f differentiating electron, so that it was assumed to be the last member of the f-block for period 6. The ground state configurations of barium and lanthanum are [Xe]6s² and [Xe]5d¹6s², respectively, so that lanthanum has a 5d differentiating electron and should be accommodated in group IIIB (group 3) as the

first member of the d-block of period 6. Moreover, the ground state of lanthanum seemed to be similar with those of the other elements of group IIIB: $[\text{Ar}]3d^14s^2$ for scandium and $[\text{Kr}]4d^15s^2$ for yttrium.

More recent spectroscopic work showed that only lanthanum, gadolinium, and lutetium have a ground state of the type $[\text{Xe}]4f^{x-1}5d^16s^2$, whereas the ground state of all the other lanthanides is $[\text{Xe}]4f^x6s^2$. Thus, the electronic configuration of Yb is $[\text{Xe}]4f^{14}6s^2$. With $[\text{Xe}]4f^{14}5d^16s^2$ representing the ground state of Lu, the differentiating electron for Lu clearly is a 5d electron. For the actinides only seven members (Ac, Pa, U, Np, Pu, Cm, Lr) have the old electronic configuration $[\text{Rn}]5f^{x-1}6d^17s^2$. The ground state configuration of thorium is $[\text{Rn}]6d^27s^2$, while that of the remaining actinide atoms is $[\text{Rn}]5f^x7s^2$. The ground state configuration of nobelium is $[\text{Rn}]5f^{14}7s^2$ while that of lawrencium is $[\text{Rn}]5f^{14}6d^17s^2$. This results in a 6d differentiating electron for lawrencium, just as was the case for lutetium. All this evidence shows that lanthanum and actinium should be considered as the first members of the f-block (not cerium and thorium), while ytterbium and nobelium should be considered as the last members of the f-block (not lutetium and lawrencium). Lutetium and lawrencium are the first members of the d-block for period 6 and 7, and should be accommodated along with scandium and yttrium in group IIIB (group 3). This also implies that the preferred representation of the medium-long form periodic table is 14LaAc (Figure 31).

It should be noted that although for decennia lanthanum and actinium could be found below yttrium in most periodic tables, some authors have placed lutetium below yttrium in the past. For instance, in the periodic table of Werner (1905a,b), there is an open place below yttrium at the position where lutetium is expected, but it should be realized that at that time lutetium had not yet been discovered (this was in 1907). However, Werner did not consider lanthanum as a homologue of yttrium, because of the differences in chemical properties between these two elements. Also in the circular system of Janet (Figure 28), the left-step table of Janet (Figure 32) and in the periodic table of Bohr (Figure 21), lutetium was placed below yttrium.

A major disadvantage of the medium-long forms of the periodic table is that the lanthanides and actinides are dissected from the main body of the periodic table and degraded to footnotes. The medium-long forms give the impression that the lanthanides and actinides are unimportant elements. This notion of unimportance is even enforced by the IUPAC notation of the groups in the medium-long form of the periodic table from 1 to 18, so that the lanthanides and actinides are not numbered at all. The long forms of the periodic table are preferred over the medium-long forms, because they give equal importance to the s-, p-, d-, and f-blocks. In this respect, the long-form of the 14LaAc table is a better conventional representation of the periodic system than the medium-long form of the 14LaAc table.

published his empirical $(n + l, n)$ rule, which correctly predicted the filling sequence in neutral atoms (Madelung, 1936):

- (1) With increasing nuclear charge Z , the orbitals are filled in order of increasing $N = n + l$.
- (2) For a fixed value of N , the orbitals are filled in the order of increasing n .

Thus, with the help of the Madelung rule, it could be explained why the 4s-orbital ($n = 4, l = 0 \rightarrow n + l = 4$) gets filled before the 3d-orbital ($n = 3, l = 2 \rightarrow n + l = 5$). Application of the Madelung rule gives rise to the data shown in Table 1. From this table, it is evident that the 4f-block starts with lanthanum (La, $Z = 57$) and ends with ytterbium (Yb, $Z = 70$). Consequently, lutetium (Lu, $Z = 71$) is the first member of the 5d-block. In analogy, one can state that the 5f-block starts with actinium (Ac, $Z = 89$), while the last member of this group is nobelium (No) with an atomic number of $Z = 102$. Finally, the next element in line, lawrencium (Lr, $Z = 103$), will start the 6d-block. Thus, according to the Madelung rule, lutetium (Lu) and lawrencium (Lr) should be placed in the third group (IIIB) underneath scandium (Sc) and yttrium (Y), whereas lanthanum (La) and actinium (Ac) should be regarded as the first representatives of the f-block elements. Therefore, only the 14LaAc table is in perfect agreement with the Madelung rule. Alternatively, one could also use Table 1 as a framework or quantum map for a new representation of the periodic system, as depicted in Figure 32. This form, known as the *Left-Step Table* or *Janet Periodic Table*, was first devised by Charles Janet in 1929 (Janet, 1929) and it offers certain advantages in comparison with the more conventional medium-long form (Bent, 2006; Katz, 2001). For example, the number of elements in the eight periods of the Janet table are given by the following sequence $\{2, 2, 8, 8, 18, 18, 32, 32\}$. Thus, due to the pairing of all the periods, one obtains the distinctive stepped profile of

TABLE 1 Application of the empirical $(n + l, n)$ rule (Madelung rule) according to which the orbitals in neutral atoms are filled in order of increasing $n + l$, and n for fixed $n + l$. The exact filling sequence is obtained by reading the quantum map from left to right, and top to bottom

$n + l$	$l = 3$	$l = 2$	$l = 1$	$l = 0$	N_{n+l}^{\max}	$Z_i \rightarrow Z_f$	$X_i \rightarrow X_f$
1	–	–	–	$1s^2$	2	$1 \rightarrow 2$	H \rightarrow He
2	–	–	–	$2s^2$	2	$3 \rightarrow 4$	Li \rightarrow Be
3	–	–	$2p^6$	$3s^2$	8	$5 \rightarrow 22$	B \rightarrow Mg
4	–	–	$3p^6$	$4s^2$	8	$23 \rightarrow 30$	Al \rightarrow Ca
5	–	$3d^{10}$	$4p^6$	$5s^2$	18	$31 \rightarrow 48$	Sc \rightarrow Sr
6	–	$4d^{10}$	$5p^6$	$6s^2$	18	$49 \rightarrow 56$	Y \rightarrow Ba
7	$4f^{14}$	$5d^{10}$	$6p^6$	$7s^2$	32	$57 \rightarrow 88$	La \rightarrow Ra
8	$5f^{14}$	$6d^{10}$	$7p^6$	$8s^2$	32	$89 \rightarrow 120$	Ac \rightarrow 120

the left-step table. This is in sharp contrast with the conventional periodic table, where the seven periods give rise to a more artificial sequence of cardinalities {2, 8, 8, 18, 18, 32, 32}. Secondly, the periods in the Janet table are characterized by a constant value of $n + l$, and this without any exception. In the medium-long form, on the other hand, it seems that the periods are characterized by a constant value of n , but this rule gets violated several times. For example, when the 3d-block unexpectedly appears in the fourth period or when all of the sudden a 4f-block emerges into the sixth period. Finally, the ordering of the blocks is more natural in the left-step table (i.e., f–d–p–s) than in the conventional long form table (i.e., s–f–d–p) since it reads s–p–d–f from right to left (in contrast to the meaningless p–d–f–s in the long-form table). An odd feature of the left-step table is the position of the noble gas helium above the alkaline-earth metal beryllium, rather than above the noble gas neon as in the conventional periodic tables. However, several arguments can be made in favor of placing helium above beryllium. For instance, the valence shell of helium ($1s^2$) is more similar to that of beryllium ($[\text{He}]2s^2$) than that of neon ($[\text{He}]2s^22p^6$).

In Table 2 both the predicted and experimentally determined electronic configurations are listed for lanthanum (La), actinium (Ac), lutetium (Lu) and lawrencium (Lr). Apparently, the Madelung rule predicts the wrong ground state configurations for lanthanum (La) and actinium (Ac). Instead of having one outer electron in an f-orbital, both lanthanum (La) and actinium (Ac) are characterized by an electron in a d-orbital outside their inert gas core. It is this fact which lies at the origin of the whole La–Ac–Lu–Lr discussion. Moreover, this is not an isolated case. In fact, it appears that for more than 30% of the transition elements, the Madelung rule predicts electronic configurations that are deviant from the empirical ones. Of course, one cannot neglect the discrepancies between the theoretically and empirically determined ground state configurations. Nevertheless, we wonder if this fact provides sufficient

TABLE 2 The theoretically predicted and experimentally observed ground state configurations of lanthanum (La), lutetium (Lu), actinium (Ac), and lawrencium (Lr)^a

Element	Z	Predicted Madelung ground state	Empirically determined ground state
La	57	$[\text{Xe}]4f^16s^2$	$[\text{Xe}]5d^16s^2$
Lu	71	$[\text{Xe}]4f^{14}5d^16s^2$	$[\text{Xe}]4f^{14}5d^16s^2$
Ac	89	$[\text{Rn}]5f^17s^2$	$[\text{Rn}]6d^17s^2$
Lr	103	$[\text{Rn}]5f^{14}6d^17s^2$	$[\text{Rn}]5f^{14}6d^17s^2$

^a The ground state configuration of lawrencium (Lr) is not empirically known, but predicted and it may not have a 6d-electron but a 6p-electron according to more recent calculations. In that case, lawrencium would form another exception to the Madelung rule.

ground to start a discussion about the correct grouping of the elements into columns. As more than 80% of all the elements are characterized by a ground state configuration that is in perfect agreement with the Madelung rule, one has every right to consider the other 19 elements (with “non-Madelung” ground states) as mere exceptions to a seemingly more general and fundamentally correct quantum rule. Actually, this is exactly the way most chemists normally behave. Hardly any chemist claims for example that the d-block should end with copper (Cu), [Ar] 3d¹⁰4s¹, palladium (Pd), [Kr]4d¹⁰, and gold (Au), [Xe]4f¹⁴5d¹⁰6s¹, because these elements are characterized by 10 electrons in a d-orbital. Consciously or subconsciously, most chemists seem to agree that these electronic configurations are exceptional, and that the d-block should end with zinc (Zn), [Ar]3d¹⁰4s², cadmium (Cd), [Kr]4d¹⁰5s², and mercury (Hg), [Xe]4f¹⁴5d¹⁰6s², as predicted by the Madelung rule.

A very unconventional way to accommodate the lanthanides can be found in a new periodic table introduced by the South-African chemist Michael Laing (2004, 2005) (Figure 33). He divides the lanthanides into three subgroups according to their important +II, +III, and +IV oxidation states: La to Sm, Eu to Tm, and Yb and Lu. In Laing’s Table, Eu and

										1											1	2				
										H											H	He				
										1.0											1.0	4.0				
2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21							
He	Li	Be	B	C	N	O	F																			
4.0	6.9	9.0	10.8	12.0	14.0	16.0	19.0																			
10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29							
Ne	Na	Mg	Al	Si	P	S	Cl																			
20.18	23.0	24.3	26.98	28.09	30.97	32.07	35.45																			
18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37							
Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr								
39.95	39.1	40.08	44.96	47.88	50.9	52.0	54.9	55.85	58.9	58.69	63.55	65.38	69.7	72.64	74.9	78.96	79.9	83.8								
38	37	36	35	34	33	32	31	30	29	28	27	26	25	24	23	22	21	20	19							
Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe								
83.8	85.47	87.6	88.9	91.2	92.9	95.9	(98)	101.1	102.9	106.4	107.9	112.4	114.8	118.7	121.8	127.8	126.9	131.3								
54	55	56	57	58	59	60	61	62	<i>Lanthanides</i>																	
Xe	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm																		
131.2	132.9	137.3	138.9	140.9	140.9	144.2	(145)	150.4																		
										63	64	65	66	67	68	69	<i>Actinides</i>									
										Eu	Gd	Tb	Dy	Ho	Er	Tm										
										162.0	157.2	158.9	162.5	164.9	167.3	168.9										
										70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
										Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
										173.0	175.0	178.5	180.9	183.0	186.2	190.2	192.2	195.1	197.0	200.6	204.4	207.2	209.0	(209)	(210)	(222)
86	87	88	89	90	91	92	93	94	<i>Actinides</i>																	
Rn	Fr	Ra	Ac	Th	Pa	U	Np	Pu																		
(222)	(223)	226.0	227.0	232.0	231.0	238.0	237.0	(244)																		
										95	96	97	98	99	100	101	<i>Actinides</i>									
										Am	Cm	Bk	Cf	Es	Fm	Md										
										(243)	(247)	(247)	(251)	(252)	(257)	(258)										
										102	103	104	105	106	107	108	109	110	111	112	113	114				
										No	Lr	Rf	Db	Sg	Bh	Hs	Mt									
										(259)	(260)	(261)	(262)	(263)	(262)	(266)	(268)									

FIGURE 33 Laing’s periodic table (Laing, 2005). Reproduced with permission from Springer.

Yb fall directly below Ba in group 2. For these elements +II is a common oxidation state. La, Gd and Lu form a column directly below Y in group IIIB. These elements have all +III as the dominant oxidation state. Ce and Tb fall in a vertical line between Zr and Hf in group 4. Ce, Tb, Zr, and Hf all have +IV as a stable oxidation state. Laing remarks that Pm falls below Tc, which is remarkable, because both are radioactive and have no long-living isotopes. From this table, it can also be derived that Am and No can easily be obtained in the +II oxidation state, and Bk in the +IV oxidation state. A weakness of Laing's table is that several elements are duplicated, so that his table is more an instrumental tool which is used to explain as many chemical properties as possible rather than being a representation of the periodic law. Moreover, Laing still adheres to Mendeleev's homologous accommodation of the rare earths. Laing (2009) also emphasized the role of gadolinium as central metal in the lanthanide series.

8. CONCLUSIONS

One notices in the alternative accommodation methodologies of the rare-earth elements, a gradual evolution going hand in hand with a growing detachment of the rare earths from the other chemical elements. Such a progression of events is easily accounted for on the basis of their unique character and perplexing properties. Mendeleev in his time was swift at discerning the primary rare-earth elements from the secondary elements, and he clearly emphasized the many consequences of the existence of primary groups within his periodic table. He thus referred to their transitional function, the apparent analogy with the transition metals, and their problematic representation within the periodic table. Mendeleev moreover explained how the presence of these primary elements resulted in both elementary characterization issues and problems of undermined periodicity. Nevertheless, throughout his lifetime, Mendeleev continuously adhered to a *homologous accommodation methodology*, thus placing the rare earths as homologues of the other elements throughout the periods of the system in the many groups I to VIII. As a consequence, all rare earths remained connected with the other elements and many chemists (Brauner in particular) eagerly tried to obtain the higher valencies of the rare-earth elements, e.g., his search for the pentavalency of didymium.

Bohuslav Brauner in 1902 pursued the detachment process by clustering the rare-earth elements within the eighth period in only one pigeon-hole of Mendeleev's system according to an *intra-periodic accommodation methodology*. In many ways, Brauner's asteroid hypothesis was analogous to the collective grouping of the transition metals in between two periods according to an *inter-periodic accommodation methodology*. Without a

doubt, both types of placement violated the concept of single occupancy, but this problem could be removed by adhering to the meta-element concept of Crookes who considered the rare-earth elements to be meta-elements of one elemental group. Brauner had revived Mendeleev's rare earth – transition metal analogy and he moreover explicated how the rare earths formed a transition from lanthanum to tantalum, thus pointing to the transitional function of primary elements. By placing the rare-earth elements in one particular group of the system (typically in groups III and IV), Brauner moreover emphasized the similarity of the rare earths metals and he resolved the problem of undermined periodicity. He also rendered their limited relationship with the other elements clear by connecting them with the congeners of one group only.

Niels Bohr concluded the detachment process by locating the rare earths as a whole in between two groups of the periodic system according to an *intergroup accommodation methodology*. He thus broke off all relations with the other elements and consequently placed the individuality of the rare-earth elements in the spotlights. Bohr furthermore removed the characterization issues by explaining the peculiar nature of primary elements on the basis of the arrangement of their innermost electrons. Moseley's investigations on X-ray spectroscopy aided as well in the resolution of the characterization problem by pointing to the existence of atomic numbers. His methods proved extremely valuable in deciding upon the homogeneity and elementarity of the rare-earth elements, and they permitted the chemical community to draw up a correct sequence of rare earths on the basis of their increasing atomic number.

The detachment process has been further emphasized nowadays by removing the rare earths from the main body and by locating them as a footnote at the periphery of Mendeleev's system. Contemporary discussions on the "rare-earth crisis" have shifted from the accommodation of the rare earths as a whole to the placement of lanthanum and lutetium in particular. Since the actinides are placed underneath the lanthanides, similar problems are posed for this group of elements and most discussions therefore center on the location of actinium and lawrencium. Chemists are thus arguing about the methods to draw the boundaries of the rare-earth island. According to the authors, the representations to be preferred are the long form of the 14LaAc periodic table and the left-step periodic table, because these do not degrade the lanthanides and actinides to footnotes of the main body of the table, and agree with the Madelung rule. The authors also discourage the use of the IUPAC numbering of the groups in the periodic table from 1 to 18, because this numbering totally neglects the existence of the lanthanides and actinides.

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