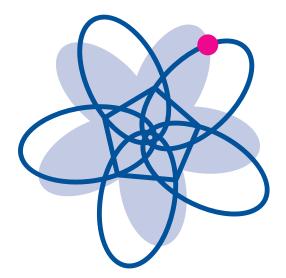
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# The Periodic Table in a National Context: Denmark, 1880-1923

Helge Kragh

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Centre for Science Studies, University of Aarhus, Denmark Research group: History and philosophy of science

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# The Periodic Table in a National Context: Denmark, 1880-1923

#### HELGE KRAGH\*

In this essay I examine how the periodic system or table was introduced in Denmark in the late nineteenth century, how it was used in chemical textbooks, and the way it was developed by a few of the country's scientists. Which were the reasons that many Danish chemists felt attracted to Mendeleev's system? It turns out that the most important reason was the predictive force of the system, in particular Mendeleev's predictions of new elements. I pay particular attention to the work of H.P.J. Julius Thomsen, which is an important example of "neo-Proutean" attempts to understand the periodic system in terms of internally structured atoms. Moreover, I direct attention to Mendeleev's connection to Danish science by way of his membership of the Royal Danish Academy of Sciences and Letters.

Thomson's speculations of composite atoms as the ultimate cause of the periodicity of the elements were vindicated by the new developments in atomic theory. A semi-quantitative explanation was offered by Niels Bohr in 1913, and in subsequent refinements of his atomic model he came close to an explanation of the entire periodic system. The essay considers Bohr's work on the periodic system in its local context, including its relation to the earlier ideas of Thomsen.

<sup>\*</sup> Centre for Science Studies, Aarhus University, 8000 Aarhus, Denmark. E-mail: helge.kragh@ivs.au.dk. This essay is an extended and revised version of a manuscript supposed to appear as a chapter in a forthcoming book on *Chemical Order in Transit* edited by M. Kaji, P. Gabor, and H. Kragh.

#### 1. The Danish chemical community, 1870-1920

In order to appreciate how the periodic system of the elements was received in Denmark, it will be helpful to provide some basic information of the country's chemical landscape.<sup>1</sup> In the period here considered, about 1870-1920, Denmark was a small country, scientifically and culturally almost completely dominated by its capital, Copenhagen. As far as chemical research and education was concerned, the most important institutions were the University of Copenhagen, the Polytechnical College, the Royal Veterinary and Agricultural College, and the Pharmaceutical College, all located in Copenhagen. The University of Copenhagen, founded in 1479, was at the time the country's only university; a second one, Aarhus University, was only established around 1930.

Although the number of chemists grew rapidly during the period, only few of them were trained at the university and even fewer had an interest in the more theoretical aspects of the chemical sciences. University-trained chemists were not only outnumbered by chemical engineers, trained at the Polytechnical College, but also by chemists with a background in medicine and pharmacy. The professionalization of chemistry manifested itself locally with the foundation in 1879 of the Danish Chemical Society, the first such society in Scandinavia. The Danish Chemical Society was broadly composed, appealing not only to professional chemists but to all "men with an interest in chemistry."<sup>2</sup>

The research interests of most Danish chemists had a practical orientation, either connected to chemical engineering or dairy products and the fermentation

<sup>&</sup>lt;sup>1</sup> For a general account of the development of science in Denmark, see Kragh et al. 2008, which includes sections on the chemical sciences. More details and references can be found in Kragh 1998 and Nielsen 2000. See also Veibel 1943, a valuable bibliography of works by Danish chemists.

<sup>&</sup>lt;sup>2</sup> Statute of October 1879, see Kragh 1998, p. 246. For details about the early phase of the Danish Chemical Society, see Nielsen 2000, pp. 92-102, and Nielsen 2008.

industry. About the turn of the century many chemists worked in the new biochemical and bio-technological sectors, where a central institution was the Carlsberg Laboratory established in 1875. Leading chemists such as Johan Kjeldahl and Søren P.L. Sørensen worked at this laboratory, which was an integrated part of the Copenhagen chemical network. Whether working with applied or pure chemistry, Danish chemists had a strong international orientation. They had typically spent some time abroad, mostly at German universities, and kept abreast of the international literature. Moreover, the large majority of them published one or more of their research articles in German or other foreign-language journals. Because of the smallness of the population, and also because the local Chemical Society did not publish its own journal, Danish chemists were forced to adopt an international attitude.

At about the time of the foundation of the Danish Chemical Society, the total number of regular academic positions amounted to only two full professors and three associate professors. These professors taught and did research at both of the twin institutions, the University and the Polytechnical College. (In addition, the Agricultural College had a professor of chemistry, Christen T. Barfoed.) Because of their small number and central positions, they were of great importance with regard to introducing and disseminating new ideas and theories from abroad. From about 1870 to the early years of the new century, academic chemistry was much dominated by two professors and powerful personalities, Julius Thomsen and Sophus M. Jørgensen. Thomsen served as a professor 1866-1901, and Jørgensen in roughly the same period, from 1871 to 1908. During the first decade of the twentieth century a much needed generation shift occurred in Danish chemistry, followed by an increased interest in theoretical and physical chemistry. With the appointment of Johannes Brønsted as professor in a new chair at the university in 1908, and Niels Bjerrum at the Agricultural College in 1914, a new era started in

Danish chemistry.<sup>3</sup> Other chemists of relevance to the subject of this essay, the periodic system, will be mentioned below.

Several chemists ended up in teaching positions, either at higher institutions (such as the Military Academy) or in the "learned" gymnasium schools attended by students who wanted to proceed to a university education. The system of "learned schools" (*Lærde Skoler*) or "Latin schools" went back to the Middle Ages, and in the seventeenth century some of them were named gymnasia. Education in these elite schools was originally dominated by Latin and other classical learning, but with a reform of 1871 it became possible also to graduate in a branch that focused on mathematical and scientific subjects. According to the 1871 educational reform, chemistry should be an obligatory part of the gymnasium curriculum, if only in modest doses and in combination with physics.

As a result of this and other reforms, several textbooks in elementary chemistry were published, either by school teachers or academic chemists. The most widely used of these books were Hannibal Jespersen's *Kortfattet Lærebog i Uorganisk Kemi* (1874) and S.M. Jørgensen's *Kemiens Begyndelsesgrunde* (1876) and *Mindre Lærebog i Uorganisk Chemi* (1888).<sup>4</sup> Another major reform followed in 1903, and according to the ministerial instruction of this reform the students should not only be taught descriptive chemistry but also elementary theoretical chemistry. The periodic system was not mentioned explicitly, which meant that teachers and textbook writers could choose to mention it or not. As we shall see, some did.

# 2. Early discussions of the periodic system

The first published recognition of the periodic system among Danish chemists I have come across dates from 1880. However, there is little doubt that many of the

<sup>&</sup>lt;sup>3</sup> Bak 1974. Nielsen and Kragh 1997.

<sup>&</sup>lt;sup>4</sup> On chemistry education and textbooks in the Danish gymnasium school system, see Riis Larsen 1998.

chemists were aware of the classification of either Mendeleev or Lothar Meyer, or both, at an earlier date. Thomsen had dealt with the groupings of the chemical elements according to their atomic weights as early as 1865, in a work that may well be counted as one of the many incomplete anticipations of the periodic system.<sup>5</sup> Thomsen's aim was not so much to establish a natural chemical classification as to defend the Proutean hypothesis, so named after the English chemist and physician William Prout, that the elements are really composite bodies made up of more elementary entities. Some twenty years later he would return to this kind of reasoning and develop it in details (see Section 4). I have not found any references in Danish chemical literature to earlier versions of the periodic system, such as those proposed by John Newlands, William Odling, and Gustavus Hinrichs.<sup>6</sup>

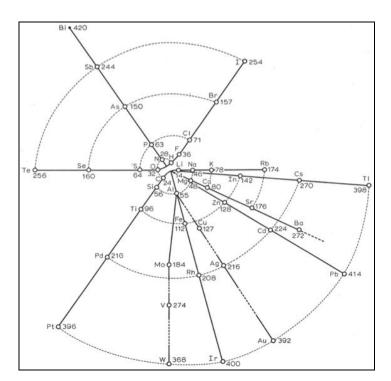


Figure 1. Hinrich's spiral periodic system of 1867, as reproduced in Van Spronsen 1969, p. 121.

<sup>&</sup>lt;sup>5</sup> Thomsen 1865. On Thomsen's speculations on composite atoms, see Kragh 1982.

<sup>&</sup>lt;sup>6</sup> On the work of these precursors, see Scerri 2007, pp. 72-92.

Hinrichs deserves mention because he was born in Holstein, which at the time was part of the Danish kingdom.<sup>7</sup> Only after the Danish-Prussian war in 1864, did Holstein become German. Born in 1836, Gustavus Detlef Hinrichs studied at the University of Copenhagen, where he most likely made the acquaintance of the ten years older Thomsen. However, after he emigrated to the United States in 1861, he seems to have had no connections to Danish chemists. Only at few occasions did he refer to Thomsen, especially to his determinations of atomic weights.<sup>8</sup> It is relevant to mention that in one of his earliest contributions to the classification of the chemical elements, dating from 1866, Hinrichs proposed atomic weight relations of the same kind that Thomsen had suggested the year before. Thus, both scientists argued that the elements in the oxygen group (Group VI) could be represented by the formula  $A = 4^2n + 7$  and those in the alkali group (Group I) by  $A = 4^2n$ , with *n* in both cases attaining the values 1, 2, 5 and 8.<sup>9</sup>

In an article of 1880 in a popular science journal, the young chemist Odin T. Christensen, at the time an assistant at the laboratory of the Polytechnical College, reviewed the recent discoveries of chemical elements, including gallium and scandium. In this connection, he discussed the place of the new elements in "the system," such as predicted by Mendeleev in the form of the hypothetical elements eka-boron and eka-aluminium. He concluded that scandium and gallium "provide strong support in favour of the view of Mendeleev, namely, that the properties of the elements and the constitution of their compounds are periodic functions of the atomic weights of the elements."<sup>10</sup> Christensen further noted that Emile Lecoq de Boisbaudran's discovery of gallium had taken place wholly independently of

<sup>&</sup>lt;sup>7</sup> The life and work of Hinrichs is described in Zapffe 1969 and Van Spronsen 1969a.

<sup>&</sup>lt;sup>8</sup> E.g., Hinrichs 1901, p. 261.

<sup>&</sup>lt;sup>9</sup> Thomsen 1865. Hinrichs 1866.

<sup>&</sup>lt;sup>10</sup> Christensen 1880, p. 421. In 1895 O.T. Christensen was appointed professor of chemistry at the Agricultural College, where he served until his death in 1914. On the significance of Mendeleev's predictions for the general acceptance of his system, see e.g. Brush 1996.

Mendeleev's prediction, which he found to be further confirmation of the essential truth of the periodic system.

Christensen was evidently impressed by the agreement between the predictions of Mendeleev and the metals discovered by Boisbaudran and Lars Frederik Nilson. When Clemens Winkler some years later discovered germanium and identified it with Mendeleev's eka-silicium, he was no less impressed: "One can scarcely think of a more striking proof of the theory of the periodicity of the elements than Mendeleev's prediction of the properties of eka-silicium, such as realized in the discovery of germanium and its compounds."<sup>11</sup>

Yet another triumph of Mendeleev's law was the outcome of the controversy concerning the correct classification of beryllium, as a homologue of either magnesium or aluminium. Based upon the empirical law of Pierre Louis Dulong and Alexis Thérèse Petit, which states that the heat capacity of a solid varies inversely with its atomic weight ( $C \times A \cong 6$  cal/degree), the atomic weight of beryllium came out as approximately 14. This value indicated that beryllium was a tervalent element, in disagreement with Mendeleev's conclusion. Only about 1880 was the element's atomic weight determined to 9.1, which largely settled the controversy. As Christensen saw it, the problem had been solved, with the new atomic weight being a "proof of the great significance that must be ascribed to Mendeleev's periodic law."<sup>12</sup>

Thomsen and Christensen were not the only Danish chemists who paid tribute to the periodic system in the 1880s. A 23-year old graduate student in chemistry, Rudolph Koefoed published in 1885 an extensive survey article on what he called the periodic law and in which he referred to Mendeleev's as well as Lothar Meyer's works of 1869-71. Like Christensen, he assigned much significance

<sup>&</sup>lt;sup>11</sup> Christensen 1886, p. 257.

<sup>&</sup>lt;sup>12</sup> Christensen 1884, p. 311. On the beryllium anomaly, see Van Spronsen 1969b, pp. 300-302.

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Figure 2. Koefoed's 1885 version of Mendelev's periodic system.

to the successful predictions of gallium and scandium. So much, in fact, that he suggested that now the chemists were on their way to establish their science on a principle nearly as universal and reliable as Newton's law of gravitation was for the astronomers.

Ironically, adding to Koefoed's confidence in the periodic system was that it – apparently – resulted in atomic weights in agreement with recent measurements. For example, it was well known that tellurium's atomic weight of 128 conflicted with the periodic system, which required a value about 125. However, as Koefoed was happy to report, recent determinations made by Bohuslav Brauner gave just this value and "thus confirm Mendeleev's prediction."<sup>13</sup> In fact, Brauner found in 1883 that Te = 127.6 but convinced himself (and apparently others) that the value was too high and due to impure tellurium. The

<sup>&</sup>lt;sup>13</sup> Koefoed 1885, p. 172, and similarly in Petersen 1890, p. 24. On the tellurium-iodine inversion problem, see Van Spronsen 1969b, pp. 238-240 and Scerri 2007, pp. 130-131. Koefoed was employed as an assistant at the Carlsberg Laboratory 1886-1890 and subsequently worked for various brewing companies.

anomaly remained a problem until about 1913, clarified only by the introduction of isotopy and the new definition of elements based on the notion of the atomic number.

## 3. The system in textbooks and education

While the periodic system seems to have been well known among Danish chemists by the mid-1880s, naturally it took some time until it percolated to the level of education and became part of the teaching of chemistry students. Julius Thomsen never wrote a textbook on chemistry, such as did his younger colleagues S.M. Jørgensen and Emil Petersen. Most university lectures in inorganic chemistry were given by Jørgensen, who however chose to ignore the periodic system. Although not opposed to the atomic hypothesis, the arch-empiricist Jørgensen, a specialist in the study of complex metal compounds, used to warn his students that atoms and molecules should primarily be conceived as convenient means of representing empirical data.<sup>14</sup> Likewise, although he may have appreciated the predictive power of the periodic system, he seems to have conceived it as somewhat speculative and neither as a necessary nor fundamental classification of the elements.

In his textbooks on chemistry, which exerted great influence on a generation of Danish chemists, Jørgensen did not so much as mention either Mendeleev or his periodic system of the elements. The system was absent from both the first and the second editions of his textbook on inorganic chemistry, published in 1888 and 1896, respectively.<sup>15</sup> Nor was the system to be found in his 1902 textbook on general

<sup>&</sup>lt;sup>14</sup> Bjerrum 1954. On Jørgensen as an empiricist, see also Kragh 1997.

<sup>&</sup>lt;sup>15</sup> Jørgensen 1888. Jørgensen, who was internationally renowned for his important work on complex metal compounds (what later became coordination compounds), received in 1906 the Lavoisier gold medal from the Académie des Sciences in Paris and in 1907 he was nominated for the Nobel Prize in chemistry by the French chemists Henri Moissan and Gaston Darboux (he did not receive the prize). See details in Kragh 1997.

chemistry, which was widely used and translated into several languages.<sup>16</sup> In this work Jørgensen included some of the more recent developments, such as the Thomsen-Berthelot theory of thermochemistry, le Chatelier's theorem of chemical equilibria, Arrhenius' and Ostwald's ideas of ionic dissociation, and Ramsay's discovery of the noble gases – but not the periodic system. He listed the chemical elements and their atomic weights alphabetically, without any indication of relations between them. The discoveries of gallium and scandium were duly mentioned, but again without mentioning their relations to Mendeleev's system. This is all the more remarkable in regard of the fact that Jørgensen also disregarded the periodic system in the second edition of 1913, where he mentioned such novelties as the liquefaction of helium, the radioactive transmutation of elements, and the electron theory of atomic constitution.

Some of these novelties were also included in the English translation of 1908. It is curious to read in Jørgensen's account of the new electron theory of matter that, "The atom is, in fact, now considered to be a nucleus of positive electricity, around which negative electrons rotate with immense velocities in definite paths, like the planets in the solar system."<sup>17</sup> This looks very much like the Rutherford-Bohr model, but is written three years before Rutherford's nuclear atom and five years before Bohr's model! The most likely explanation is that Jørgensen was aware of the planetary atomic model that the Japanese physicist Hantaro Nagaoka published in 1904, and that he mistakenly thought that this kind of model was generally accepted. In fact, by 1908 the only atomic model that enjoyed wide recognition was J.J. Thomson's "plumcake" model where the electrons moved in an extended

<sup>&</sup>lt;sup>16</sup> Jørgensen 1902, with translations into German (1903), Greek (1904), Italian (1904), and English (1908). The English translation (Jørgensen 1908), an extended version of the German translation, received a critical review in *Nature* 79 (1908), 218.

<sup>&</sup>lt;sup>17</sup> Jørgensen 1908, p. 26.

positive and massless charge of atomic dimension. The suggestion receives support from a passage in the Danish (but not the English) text, where he spoke of

... a nucleus made up of positive electrons. ... Thus, in atoms of considerable weight, such as uranium with a weight of about 240 times that of hydrogen, one must assume the existence of several hundred thousands of electrons.<sup>18</sup>

Jørgensen's comments are of some interest because it may be the first time that the positive central charge was called a "nucleus." Neither Nagaoka nor Rutherford in 1911 used this term. In any case, his mention of atomic theory may indicate that he was not, after all, a narrow empiricist disregarding the theoretical aspects of chemistry and physics.

The absence of the periodic system in Jørgensen's book was noted in an otherwise positive review in the German periodical *Naturwissenschaftlicher Rundschau*:

Neither the periodic system of the elements nor the related question of a primary matter is mentioned in the book. The reviewer is unaware of the author's reason for this reservation, but it seems to him [the reviewer] that this question – which possibly goes deeper into the philosophical foundation of chemistry than any other subject – might well have fitted into the book.<sup>19</sup>

The first university-level textbook to incorporate the periodic system, written by Odin Christensen in connection with his lectures at the university, appeared in 1890 and ran through four editions. Without mentioning Mendeleev by name, he introduced his system in the form of an appendix, not as an organizing principle

<sup>&</sup>lt;sup>18</sup> Edition of 1913 of Jørgensen 1902, on p. 30.

<sup>&</sup>lt;sup>19</sup> Review by "R.M." in Naturwissenschaftlicher Rundschau 19 (1904), 271.

for treating the properties of the elements.<sup>20</sup> Using "periodic system" interchangeably with "periodic law," his main justification for the classification was its ability to predict new elements in accordance with later experiments.

Another advocate of the periodic system was Emil Petersen, who after studies in Paris and Leipzig had taken up the new physical chemistry of the Ostwald school. In 1889 he gave a lecture series at the University of Copenhagen on the rarer elements, with special emphasis on the problem of their places in the periodic system. By that time he was convinced of the basic truth of the system and also that it reflected an underlying unity of matter.<sup>21</sup> After having been appointed professor of chemistry in 1901, he wrote a textbook in inorganic chemistry in which he included a fairly detailed account of the system.

According to Petersen, the periodic system was a useful classification, yet "it is far from a perfect expression of the facts [and] ... many deficiencies are attached to it." Among these deficiencies he mentioned the Ar-K and Te-I atomic weight inversions, and he also found it problematic that copper and mercury ("which chemically are so analogous") were placed in different groups. On the other hand, he was convinced of the importance of the periodic system, not least because "in several cases the existence of elements and their main properties were predicted in advance, many years before they were actually discovered." Rather than mentioning the classic cases of gallium, scandium and germanium, he called attention to the new element radium, the atomic weight of which had recently been determined by Pierre and Marie Curie in Paris. As Petersen pointed out, radium "is very similar to barium and, with an atomic weight of 225, it fits nicely into the system."<sup>22</sup>

<sup>&</sup>lt;sup>20</sup> Christensen 1890, with later editions of 1896, 1902 and 1908.

<sup>&</sup>lt;sup>21</sup> Petersen 1890. On his lectures series, see Jensen 1983, p. 511.

<sup>&</sup>lt;sup>22</sup> Petersen 1902, pp. 317-321. A second edition of the book appeared in 1906.

Some of the features of the textbooks of Christensen and Petersen can also be found in the university textbooks of the next generation of Danish chemists: Although the periodic system was now included, it played no great role and did not function as a principle for organizing the discussion of the elements and their compounds. The two new professors of the 1910s, J. Brønsted and N. Bjerrum, each wrote a textbook in inorganic chemistry, intended to supplement their lectures at the University and the Agricultural College, respectively. Whereas Brønsted's book of 1916 still based the periodic system on atomic weights, Bjerrum's work of the following year incorporated the most recent developments in atomic physics.<sup>23</sup> This was the first time in Danish chemistry that the atomic number (Z) appeared as an ordering parameter for the elements, and also the first time that the Rutherford-Bohr nuclear model was introduced as a way of explaining the periodic system in terms of atomic structure. But apart from this novelty, Mendeleev's system played no prominent part in the book.

In the period under consideration, the custom in Denmark was to use textbooks written by local authors, in most cases the professors. Textbooks translated from other languages were not, or only very rarely, used either at the University or elsewhere. Nor were German or other papers from abroad on the periodic system translated into Danish.

Among the elementary textbooks intended for the gymnasium schools that appeared in the early part of the twentieth century, some referred to or made use of the periodic system. This was the case with a book written by Julius Petersen, a polytechnically trained chemist and former assistant of S.M. Jørgensen, who in 1908 was appointed professor of chemistry at the University of Copenhagen. Petersen followed the tradition by emphasizing the successful predictions of elements based on Mendeleev's system, and at the same time he, much like his colleague and

<sup>&</sup>lt;sup>23</sup> Brønsted 1916. Bjerrum 1917, pp. 214-215.

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Figure 3. Rasmussen's periodic system of 1912, a version of the table originally proposed by Julius Thomsen.

namesake Emil Petersen, pointed to its incompleteness and problems such as the Ar-K and Te-I atomic weight anomalies. Another book for the gymnasium, written by the teacher Hans Rasmussen, is noteworthy because it presented the periodic system in the unconventional form suggested by Julius Thomsen, with vertical groups and horizontal periods (Figure 3).<sup>24</sup> The pedagogical value of the system was not always appreciated, and some teachers suggested that it, being too theoretical, should not be part of the curriculum.<sup>25</sup> It took until 1958 before the periodic system became a formally required part of the Danish gymnasium education system.

<sup>&</sup>lt;sup>24</sup> Petersen 1907. Rasmussen 1912.

<sup>&</sup>lt;sup>25</sup> Berg 1939.

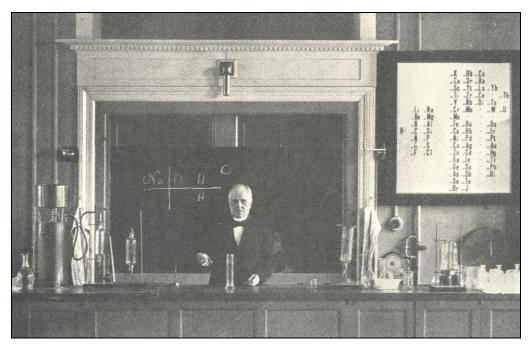


Figure 4. Julius Thomsen teaching in front of his periodic table.

# 4. Speculations on the complexity of atoms

A pioneer of thermochemistry, Julius Thomsen was first and foremost an experimentalist. Yet he also had an abiding interest in chemical theories, and he was the only Danish scientist who, until Bohr in 1913, actively examined and contributed to the understanding of the periodic system. As mentioned, ever since the 1860s he entertained the heterodox view that the atoms of chemistry are complex particles and that this is revealed by regularities in their atomic weights. Of course, he was far from the only neo-Proutean of his time, but he was one of the most distinguished and articulate advocates of the idea of a basic unity of matter. In a work of 1887 he connected for the first time this idea with the periodic system, undoubtedly inspired by a remarkable address that William Crookes had given the year before to the British Association for the Advancement of Science.<sup>26</sup>

Thomsen was particularly concerned with the question of why only some atomic weights are realized in nature, while other possible weights seem to be missing. An ardent advocate of so-called inorganic Darwinism, he thought that the answer was to be found in the slow evolution of elements from simple to more complex structures. "The right of the fittest has manifested itself and only allowed the formation of atoms with a structure firm enough for a continuous existence," he wrote.<sup>27</sup> As to Mendeleev's system, he praised it for its ability to identify missing elements and predict their properties, such as had been the case with the famous trio of gallium, scandium and germanium. Contrary to Mendeleev and most other chemists, he was convinced that the system was a key to understand the complexity of the elements and that it would eventually be possible to represent it as a mathematical function of the atomic weight. The version of the periodic system he presented in 1887 was fairly orthodox, not differing significantly from Mendeleev's. Like the Irish chemist Thomas Carnelley had done the year before, Thomsen suggested an analogy between the chemical elements and the hydrocarbon radicals.28

The questions addressed by Thomsen were taken up also by Emil Petersen, who in 1890 discussed the nature of the chemical elements and the idea of a basic unity of matter such as discussed by Crookes and others.<sup>29</sup> Evidently in sympathy with the idea, he suggested that it received support from the periodic system. "It is hardly to doubt," he wrote, "that in this way we will eventually get insight into the

<sup>&</sup>lt;sup>26</sup> Thomsen 1887. Crookes 1886. Although Thomsen did not refer to Crookes' address, it is evident that he knew about it.

<sup>&</sup>lt;sup>27</sup> Thomsen 1887, p. 37. On Thomsen's neo-Prouteanism and inorganic Darwinism, see Kragh 1982 and Kragh 2009a.

<sup>&</sup>lt;sup>28</sup> Thomsen 1887, p. 22. Carnelley 1886.

<sup>&</sup>lt;sup>29</sup> Petersen 1890. Contrary to Thomsen, Petersen referred explicitly and in great details to Crookes' address, which clearly impressed him.

unity that lies behind the varied diversity of the elements." Referring to Mendeleev's recent Faraday lecture, he admitted that the dream of a primary matter was somewhat speculative, but he nonetheless found the dream worthy of pursuit.<sup>30</sup> Whether in Mendeleev's or Meyer's version, Petersen thought highly of the periodic law, which he summarized in the formula "The properties of the elements stand in a periodic relationship to the atomic weight." He explained that there were two major reasons for accepting the truth of the law, the one relating to its unifying power and the other to its predictive power:

It is the merit of the periodic law that it has arranged all known elements – and in some cases also unknown elements – in one coherent system and demonstrated the intimate mutual relationship between their properties. It has assigned the right place for some elements whose relationships to other elements were doubtful. For some of the less well known elements it has proved possible, by means of the table, to correct their atomic weights such as found experimentally. ... These and other applications of the system are of considerable scientific importance. Another application of the system is less important, but on the other hand more striking and amazing, namely, its ability to predict as yet undiscovered elements – to predict their existence and most important properties years before there were actually discovered and manufactured.<sup>31</sup>

That is, according to Petersen the scientific value of the periodic law was primarily its ability to arrange the elements into a coherent system, whereas he gave lower priority to its predictive power. No other Danish chemist expressed a similar view.

To return to Thomsen, in a memoir of 1894 published by the Royal Danish Academy of Sciences, he offered a detailed examination of the atomic weights and

<sup>&</sup>lt;sup>30</sup> Mendeleev's paper in the *Journal of the Chemical Society,* in which he rejected the hypothesis of a unity of matter and denied that is was supported by the periodic law, has been reprinted several times. See, e.g., Jensen 2002, pp. 162-188.

<sup>&</sup>lt;sup>31</sup> Petersen 1890, pp. 22-23.

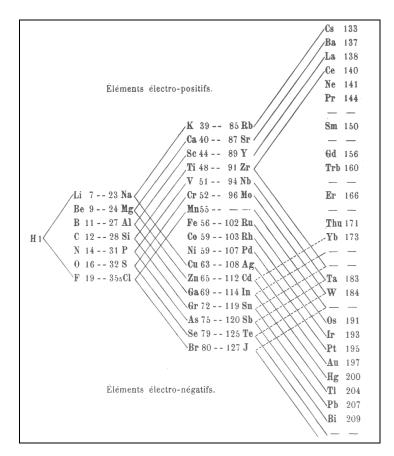


Figure 5. Thomsen's periodic system of 1895.

their significance. His purpose was to establish that they, if only properly interpreted, revealed that "the so-called atoms of our elements have evolved out of combination of particles of a common basic substance."<sup>32</sup> He did not on this occasion discuss the relation to the periodic system, but this is what he did the following year, in a paper in which he proposed a new classification of the elements.<sup>33</sup> From a formal point of view, Thomsen's innovation was merely to reverse periods and groups, which was not entirely original since versions of this kind had been proposed earlier, first by Thomas Bayley in 1882 and again by Carnelley in 1886.<sup>34</sup> However, in 1894 Thomsen was unaware of these two systems,

<sup>&</sup>lt;sup>32</sup> Thomsen 1894, p. 324.

 <sup>&</sup>lt;sup>33</sup> Thomsen 1895a. The paper also appeared in German, in *Zeitschrift für anorganische Chemie* 9 (1895), 190-193, and was translated into English in *Chemical News* 71 (1895), 89-91.
<sup>34</sup> Bayley 1882. Carnelley 1886.

such as he stated in a letter to the American chemist Francis Venable, who in a book of 1896 described Thomsen's system in some detail.<sup>35</sup>

Thomsen designed his version of the periodic system (Figure 5) in such a way that it immediately suggested a common origin of the elements, that is, an evolutionary interpretation. Irrespective of such an interpretation, it included several novel features and indicated the existence of possible new elements. For example, it was the first version of the periodic system that included the correct number of rare earth metals, namely 14, and placed this group between cerium and an unknown element of atomic weight 180 with chemical properties analogous to those of zirconium. This hypothetical element – later identified as hafnium – also implicitly appeared in Mendeleev's original periodic system of 1869, but it was only with Thomsen that it was given explicit attention and placed outside the rare earth group.<sup>36</sup>

Another feature of Thomsen's brief paper deserves mention, namely the "curious fact" that the number of elements in the periods is 1, 7, 17 and 31. These numbers, Thomsen pointed out, can be written as  $1, 1 + 2 \times 3, 1 + 2 \times 3 + 2 \times 5$ , and  $1 + 2 \times 3 + 2 \times 5 + 2 \times 7$ . Expressed slightly differently, the number of elements follows the expression

$$N=2n^2-1,$$

or, if the inert gases are included,  $N = 2n^2$ . "Is this relation more than a coincidence," Thomsen asked, cautiously answering that, "Only the future will show, but I have nevertheless wished to expose the possibility of a more profound

<sup>&</sup>lt;sup>35</sup> Venable 1896, pp. 209, 271-276.

<sup>&</sup>lt;sup>36</sup> On the complex question of the position of the rare earth metals in the periodic system, see Thyssen and Binnemans 2011, who however fail to notice Thomsen's contribution.

cause."<sup>37</sup> He probably referred to a systematic arrangement of the proto-atoms of which he assumed the elements to be built up, such as he had indicated in his essay of 1887. The numerical law suggested by Thomsen came to be known as Rydberg's rule, named after the Swedish spectroscopist Janne (Johan Robert) Rydberg who proposed it in different forms in works of 1906 and 1913.<sup>38</sup>

Apparently Rydberg was unaware of Thomsen's earlier speculation, and so was (with the exception of Bohr) the new generation of atomic physicists in the tradition of quantum theory. It was their work which eventually resulted in a rational explanation of the rule, namely in terms of quantum mechanics and the Pauli exclusion principle. Thus, at the Rydberg centennial conference in Lund, Sweden, in 1954, Wolfgang Pauli, referring to a paper by Rydberg of 1897, erroneously stated that, "At that time no sufficient attention had been paid to Rydberg's claim and only later the work of Julius Thomsen and others on the periodic system of the elements followed."<sup>39</sup>

Apart from his inclination to numerology, Thomsen had no good reason to take his "curious fact" seriously, and apparently he soon lost whatever confidence he may have had in it. The periodic system that he used in his lectures at the University of Copenhagen in about 1898 differed in some respects from the published one, especially by having the long period of 31 elements replaced by three new and smaller periods.<sup>40</sup> Moreover, he placed the inert gases in such a way that the new system no longer revealed the  $2n^2$  relationship.

<sup>&</sup>lt;sup>37</sup> Thomsen 1895a, p. 136. He further noted that 1, 3, 5, and 7 were all prime numbers, but suggested that this was probably a coincidence.

<sup>&</sup>lt;sup>38</sup> On Rydberg's elaborated and controversial version of the periodic system, see Rydberg 1906. In her valuable study of Rydberg, Sister St. John Nepomucene states, erroneously, that Rydberg in 1906 was the first to recognize the  $2n^2$  relationship. Nepomucene 1960, p. 141.

<sup>&</sup>lt;sup>39</sup> Pauli 1994, p. 75.

<sup>&</sup>lt;sup>40</sup> The original periodic table, as used by Thomsen in 1898 and for several years by other lecturers of chemistry in Copenhagen, is preserved at the Technical Museum in Elsinore.

#### 5. The position of the inert gases

It is well known that the discovery of argon in late 1894, and also of helium half a year later, caused a major problem for the periodic system. The problem was not only that there was no natural place for argon, but also that the new gas appeared to be mono-atomic and with an atomic weight of 39.9, greater than the one of potassium.<sup>41</sup> However, the crisis disappeared and was turned into a triumph when it was realized that the new inert gases could be added as a separate group of zero-valence elements. This was an important test for the still young periodic system, and it has been suggested that the successful incorporation of the inert gases was of no less importance for the authoritative status of the system than the earlier predictions of metallic elements.<sup>42</sup>

The problems that emerged with the discovery of argon were known among Danish chemists and reflected in their works. It were these problems that induced Thomsen to "publish some ideas, with which I have been occupied for years, but which I have wished not to publish until now, because I would not encumber science with unverifiable hypotheses."<sup>43</sup> The ideas he referred to were probably mathematical relations between the electrochemical character of the elements and their atomic weights. From such considerations Thomsen argued that there supposedly existed a new group of chemical elements that were electrochemically indifferent and possessed zero valence. As to the significance of these elements for the hypothesis of a common constitution of the atoms, he wrote:

<sup>&</sup>lt;sup>41</sup> On this problem, see Hirsch 1981 and Carmen 2001.

<sup>&</sup>lt;sup>42</sup> Scerri 2007, p. 156.

<sup>&</sup>lt;sup>43</sup> Thomsen 1895b, p. 283, with English translation in *Chemical News* 77 (1895), 120-121. According to the English chemist Edward Thorpe, the paper was of great importance because it foreshadowed the discovery of the congeners of argon. Thorpe 1910, p. 170.

If one assumes the hypothesis of the unity of matter which, despite all attacks, cannot be displaced from the minds of scientists, one finds that the hypothetical inactive elements must have been formed by a regular and closed arrangement of the prime atoms, in such a way that the equilibrium of the molecules thereby formed have no disturbing points of action for chemically active substances; therefore they would not be able to form stable compounds but would only follow the general laws of gravity.<sup>44</sup>

Moreover, based on his new and still unpublished periodic system he suggested that the atomic weights of the elements – of which only argon was known at the time – were 4, 20, 36, 84, 132, and 212. These figures were not wide off the mark, cp. that He = 4, Ne = 20, Ar = 40, Kr = 84, Xe = 131, and Rn = 222. For the seventh period he proposed that it would end with a noble-gas element of atomic weight 292. Like several other scientists at the time, Thomsen searched for a mathematical representation of the periodic system, and he thought that his new extension of the system was a step in the right direction.

In his essay of 1887, Thomsen speculated that the hypothetical solar element, helium, might be a subhydrogenic primary element, that is, with an atomic weight smaller than 1 (Crookes did the same in his 1886 address). When he read his paper on the inert gases to the Royal Danish Academy on 19 April 1895, William Ramsay had not yet announced his discovery of helium in terrestrial sources. Helium initially raised questions with regard to its place in the periodic system, not least because it initially looked like being a twin element: based on its peculiar spectrum helium was suspected to consist of two elements, one with an atomic weight about 5 and another ("parhelium") with atomic weight 3.<sup>45</sup> According to Henry Wilde, an English physicist and astronomer, "There is absolutely no place in Mendeleef's

<sup>&</sup>lt;sup>44</sup> Thomsen 1895b, p. 286.

<sup>&</sup>lt;sup>45</sup> Parhelium was supported by Rydberg, who assigned it the chemical symbol Pa, while Brauner speculated that it might be triatomic hydrogen, H<sub>3</sub>. On the early history of helium, both astronomical and terrestrial, see Kragh 2009b.

system for elements with atomic weights between lithium and hydrogen, as the Russian chemist never contemplated the existence of elements with properties and cosmic relations as the new gases have been found to possess."<sup>46</sup> However, it was soon realized that the new inert elements did not pose a problem for Mendeleev's system: argon and helium belonged to a new group, in agreement with Thomsen's proposal.

Thomsen kept an interest in the inert gases, and in 1898 he succeeded to detect helium in a red fluorite mineral in Greenland. In the same year he gave an address to the 15th Scandinavian Meeting of Natural Scientists, held in Stockholm, in which he emphasized the scientific importance of what appeared to be a new group of gases belonging to the periodic system.<sup>47</sup>

Thomsen was not the only Danish chemist with an interest in the new gases. In a survey article addressed to Scandinavian pharmacists of June 1895, Emil Petersen discussed the sensational discovery made by Ramsay and Lord Rayleigh. In agreement with the "two distinguished British chemists" – to his dismay, Rayleigh was often thought to be a chemist – he concluded that the evidence spoke in favour of argon being mono-atomic and with an atomic weight close to 40. He was confident that there was no fundamental disagreement between argon and Mendeleev's system:

As soon as a new element is discovered and a determination of its atomic weight has been obtained, what is usually done is to look at Mendeleev's well known periodic system. All known elements have been secured a place in this system, as determined by their atomic weights and in agreement with the element's physical and chemical properties.<sup>48</sup>

<sup>&</sup>lt;sup>46</sup> Wilde 1895, p. 471.

<sup>&</sup>lt;sup>47</sup> Thomsen 1898a. Thomsen 1898b.

<sup>&</sup>lt;sup>48</sup> Petersen 1895, p. 238.

After having discussed various solutions to the problem of argon's place in the system, he ended up with suggesting that the standard version of Mendeleev's system was probably incomplete. Later the same year, the delicate question was reviewed in detail by S.P.L. Sørensen, Thomsen's and Petersen's colleague at the Carlsberg Laboratory and later famous for his invention of the pH scale. Sørensen expressed strong support of Thomsen's view of the periodic system and its "convincing argument for the existence of a group of elements of an inactive character."<sup>49</sup>

### 6. From Thomsen to Bohr

At about the time when Mendeleev and Thomsen passed away (in 1907 and 1909, respectively), there was increasing evidence that the periodic system was a manifestation of the internal structure of atoms, such as Thomsen and other neo-Prouteans had speculated. This was an important feature of J.J. Thomson's atomic model, according to which atoms were conglomerates of electrons structured in concentric circles and moving in an imponderable positive charge of atomic dimension. Indeed, as early as 1897, in the paper in which he announced the discovery of the electron (or "corpuscle," as he insisted to call it), Thomson explicitly referred to rings of electrons as an explanation of Mendeleev's system.<sup>50</sup> However, by 1910 the Thomson model had run out of power, to be replaced a few years later by the highly successful quantum theory of the nuclear atom. Nonetheless, the general idea that the periodicity of the elements reflected the configurations of the electron survived the demise of the Thomson model. It is worth pointing out that according to Thomson the periodicity was due to similar configurations of internal rings of electrons, not a similarity of the outer configurations close to the surface of the atom.

<sup>&</sup>lt;sup>49</sup> Sørensen 1896, p. 17.

<sup>&</sup>lt;sup>50</sup> On this and other early explanations of the periodic system, see Kragh 2001.

Young Niels Bohr was well acquainted with general chemistry, including the periodic system in the versions of both Mendeleev, Meyer and Thomsen, which he had been taught in lectures in inorganic chemistry held at the University of Copenhagen in 1905.<sup>51</sup> The lecturer was the young chemist Niels Bjerrum, who was familiar with the recent attempts to explain the periodicity of the elements in subatomic terms. In an article of 1907, Bjerrum reviewed these ideas, including the view that the atomic weights reflect the internal composition of the atoms. He concluded that "the law-like connection between the properties of the elements and their atomic weights, such as expressed in the periodic system, can hardly be explained without assuming an internal constitution of the atom."<sup>52</sup> This was not an original observation, but at the time it was unusual for chemists, whether in Denmark or elsewhere, to relate the periodicity of the elements to their internal structure.

Although Bohr's great work of 1913 focused to a large extent on the hydrogen atom, he also dealt with the electron structures of more complex atoms. As he wrote in a letter of February 1913 to George von Hevesy, his still unpublished theory would include a "very suggestive indication of an understanding of the periodic system of the elements."<sup>53</sup> Contrary to earlier physicists and chemists, Bohr could make use of the Dutchman Antonius van den Broek's very recent introduction of the atomic number – corresponding to the charge of the atomic nucleus – as the ordinal number of the periodic system. Taking advantage of this new definition of a chemical element, and also of the periodic variation of the atomic volume of the elements, he ventured to suggest electron configurations for

<sup>&</sup>lt;sup>51</sup> The role of chemistry in Bohr's atomic theory is discussed in Kragh 1977. See also Kragh 2012.

<sup>&</sup>lt;sup>52</sup> Bjerrum 1907, p. 77.

<sup>&</sup>lt;sup>53</sup> Quoted in Bohr 1981, p. 530.

the first 24 elements, from hydrogen to chromium. His proposal of electron rings in these atoms was this:<sup>54</sup>

Η	1 (1)	F	9 (4, 4, 1)	Cl 17 (8, 4, 4, 1)
He	2 (2)	Ne	10 (8, 2)	Ar 18 (8, 8, 2)
Li	3 (2, 1)	Na	11 (8, 2, 1)	K 19 (8, 8, 2, 1)
Be	4 (2, 2)	Mg	12 (8, 2, 2)	Ca 20 (8, 8, 2, 2)
В	5 (2, 3)	Al	13 (8, 2, 3)	Sc 21 (8, 8, 2, 3)
С	6 (2, 4)	Si	14 (8, 2, 4)	Ti 22 (8, 8, 2, 4)
Ν	7 (4, 3)	Р	15 (8, 4, 3)	V 23 (8, 8, 4, 3)
0	8 (4, 2, 2)	S	16 (8, 4, 2, 2)	Cr 24 (8, 8, 4, 2, 2)

In this way he explained the chemical similarity between elements of the same group as due to the same number of electrons in the outermost ring. However, he cautiously avoided to identify explicitly the electron structures with definite chemical elements.

Bohr's 1913 explanation of the periodic system was incomplete and wrong in its details, but nonetheless a great progress compared to earlier attempts. It was a first step toward the much fuller and more detailed theory he composed in 1921-1923, still based on the semi-classical so-called old quantum theory in which electrons moved along definite orbits. In this important theory, he made use of a slightly modified version of Thomsen's table with vertical periods and horizontal groups. Thus, in an address of 1921 on the periodic system he said that he preferred the graphic version "proposed more than twenty years ago by Julius Thomsen, … [because it] is more suited for comparison with theories of atomic constitution."<sup>55</sup>

<sup>&</sup>lt;sup>54</sup> Bohr 1913, p. 497, reprinted in Bohr 1981.

<sup>&</sup>lt;sup>55</sup> Quoted in Bohr 1977, p. 272. A similar reference to Thomsen's periodic table appeared in Bohr's article on "Atom" in the 14th edition (1929) of the *Encyclopedia Britannica* (Bohr 2007, pp. 42-48).

Likewise, when he gave his Nobel lecture in Stockholm in December 1922, he used the occasion to pay tribute to the Danish chemist.

Like Thomsen, Bohr ambitiously suggested an extension of the periodic system to cover also the unknown transuranic elements. For example, he offered a full electronic configuration of the element Z = 118, which he supposed was an inert gas inert gas homologous to radon. As mentioned, Thomsen had speculated that the same hypothetical element had an atomic weight of about 292.

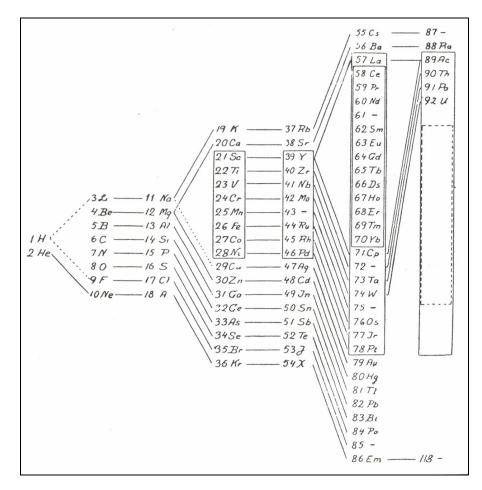


Figure 6. The Bohr-Thomsen system, as Bohr discussed it in his Nobel lecture in Stockholm in December 1922.

#### 7. Conclusion: Mendeleev and the Royal Danish Academy

Although dating from 1869, Mendeleev's periodic system was only explicitly noticed by Danish chemists about a decade later. By the mid-1880s it seems to have been broadly known and also accepted as a useful classification by many chemists. The delay in the reception was not unusual, if compared with other small countries, and it does not indicate any particular backwardness of chemistry in Denmark. The system or law was considered of interest only by relatively few chemists, whereas it tended to be ignored by the majority who worked within the more practical fields of chemistry, such as related to engineering, pharmacy and dairy products. Generally speaking, one should be careful not to confuse lack of references in the literature with ignorance: Although the periodic system was not mentioned very frequently by Danish chemists, this does not mean that it was unknown or considered unimportant.

One indication of the status that Mendeleev, and by implication the periodic system, enjoyed in Denmark is that on 5 April 1889 the Russian chemist was elected a foreign member of the Royal Danish Academy of Sciences and Letters.<sup>56</sup> Julius Thomsen served at the time as president of the Academy, and it appears to have been on his initiative that Mendeleev was invited to become a member of the prestigious society going back to 1742. (The slightly older Royal Swedish Academy of Sciences, founded in 1739, elected Mendeleev a member in 1905). The letter of motivation was written by Thomsen and signed jointly by him and S.M. Jørgensen.

<sup>&</sup>lt;sup>56</sup> The invitation was confirmed at the next meeting of the Academy, on 26 April 1889. See Lomholt 1942, p. 407, and *Oversigt over det Kongelige Danske Videnskabernes Forhandlinger* (1889), p. 44 and p. 46. Mendeleev was awarded the Davy Medal by the Royal Society of London for 1882, and the next year the same honour was bestowed on Thomsen (in both cases they shared the prize, with Lothar Meyer and Marcellin Berthelot, respectively). While Mendeleev was elected a foreign member of the Royal Society in 1892, Thomsen was elected a member ten years later.

Given Jørgensen's lack of appreciation of the periodic system, one may assume that the proposal was actually due to Thomsen. At any rate, Denmark's two leading chemists, both of them of international repute, motivated their proposal as follows:<sup>57</sup>

During many years, Prof. Mendeleev has conducted a great number of excellent investigations, in part of a general chemical nature and in part of a physico-chemical nature, and they have all be characterized by a superior mind. It would be too long-winded to recount the subjects of all these investigations, but we would like to emphasize his great works on the dependence of gases on temperature and pressure. However, Mendeleev's name has become even more generally known by his brilliant work on the theory of how the chemical and physical properties of the elements depend on their atomic weights – the so-called periodic system. In this way he has opened a wide field for a philosophical discussion of the most important chemical phenomena; his theories has several times been remarkably confirmed by the discovery of elements whose existence and most important properties he had predicted as a consequence of the system. Objections can indeed be raised against the full justification of the system, such as can be done against many other theories; but the system has, to a very high degree, advanced chemistry as a science, and for this reason Mendeleev's name will for ever be inscribed among the first in the history of chemistry.58

Mendeleev quickly responded to the invitation, expressing how great an honour it was for him to become a foreign member of the Royal Danish Academy. He was

<sup>&</sup>lt;sup>57</sup> Letter in Thomsen's handwriting to the Academy's secretary of 25 February 1889. In Danish, author's translation. Archive of the Royal Danish Academy of Science.

<sup>&</sup>lt;sup>58</sup> During the 1870s Mendeleev conducted extensive investigations on the compressibility of gases, which led him to suggest a generalization of the ideal gas laws (Gordin 2004, chapter 3). This work, completely overshadowed by his research on the periodic system, was not seen as particular important, but apparently Thomsen and Jørgensen thought that it was. It is not unreasonable to assume that the reference to Mendeleev's work on gases reflected Jørgensen's view of the relative significance of the work of the Russian chemist.

pleased to accept this sign of "the scientific brotherhood of the peoples," which he considered a manifestation of "the sympathy which unites the Danes and the

Monsieur, Ayant ou l'honneur insigne d'être els Membre de l'Académie Regale Danoide des Sciences et des Littres, je ser possuade que je le tris à la frateenite sciendifique de peuples, qui m'a choisi pour abjet de se manifestation en raison Ala symposithic qui unit do Lunis les Russes. Te Vous price, Mansiour, de voulair dien transmettre a vottre savante Assemblee les sentiments de la profende gratitale, dent je suis gainette! Agriez, Monsine, l'expension des sentiments Diskingnes, avec lisquels j'ai l'lonneur d'être Votre this humble of a hissant serviteur D. Mendeleeff.

Figure 7. Mendeleev's letter to the Royal Danish Academy of 1889.

Russians."<sup>59</sup> Mendeleev's mention of the special Danish-Russian relationship was probably a reference to princess Dagmar, the daughter of the Danish king Christian IX and, as Empress Maria Feodorovna, the wife of Russia's Tsar since 1881, Alexander III. Mendeleev was a loyal and appreciated consultant of the Tsar's administration.<sup>60</sup>

As seen from the perspective of Danish chemists, the periodic system was of importance primarily because of its successful predictions of new elements. It was this feature which provided the system with a measure of credibility and authority. Because the predictions were associated with Mendeleev and his version, rather than the versions of Meyer and others, the periodic system was invariably associated with the name of the Russian chemist. Whereas the periodic system did

 <sup>&</sup>lt;sup>59</sup> Mendeleev to Hieronymus G. Zeuthen, secretary of the Royal Danish Academy, of 14
April 1889. In French. Archive of the Royal Danish Academy of Science.
<sup>60</sup> Gordin 2004, chapter 6.

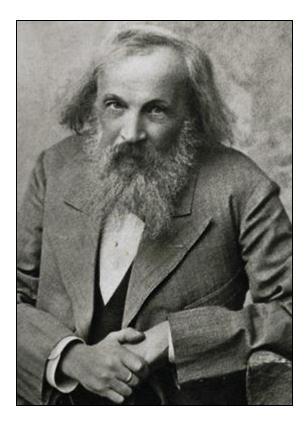
not appear prominently in Danish academic textbooks in chemistry between 1880 and 1900 – and in some cases did not appear at all – it was introduced in elementary textbooks at a relatively early date. By 1910, most Danish students in the gymnasium schools would have encountered the system, if only in its most rudimentary form. On the other hand, both in university and gymnasium level textbooks it typically appeared isolated from the systematic description of the elements and their properties.

Education apart, only one Danish chemist took an active scientific interest in the periodic system of the elements. During the 1890s Julius Thomsen did important work on its interpretation, which to him was to be found in terms of the complex structure of atoms. Although Thomsen's contributions to this area of speculative chemistry were well known internationally, and although they to some extent served as an inspiration for Bohr's later work, they did not make much of an impact on Danish chemistry. Emil Petersen shared some of his ideas, but on the whole Thomsen was a lone figure in his advocacy of neo-Proutean speculations. About 1900, the view of most Danish chemists may have been something like this: Sure, the periodic classification of the elements is an interesting hypothesis with a certain predictive power, but scarcely more than that; it is probably not of fundamental importance, nor is it necessary for understanding inorganic chemistry; in any case, it has little to do with what most chemists are occupied with, namely practically oriented experiments.

Given the vast difference in the amount of consulted sources, whether textbooks or articles, it is problematic to compare the case of Denmark with Stephen Brush's much more detailed study of the reception in the United States and Britain. Nonetheless, I think two comments may be appropriate. First, among Danish chemists the prediction of new elements was generally given more attention than the correlation between the physico-chemical properties and atomic weights.

This is contrary to what Brush found in his survey. Second, Brush observes that in chemistry textbooks the periodic system was "not as a rule introduced at the beginning or used as an organizing principle for those books."<sup>61</sup> This conclusion fully agrees with my more limited study of the Danish case.

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<sup>&</sup>lt;sup>61</sup> Brush 1996, p. 612.

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