

# A review of research on the history and philosophy of the periodic table

## Una revisión de investigaciones sobre la historia y la filosofía de la tabla periódica

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### Abstract

*The article summarizes the present state of research into the conceptual foundations of the periodic table. We give a brief historical account of the development of the periodic table and periodic system, including the impact of modern physics due to the discoveries of Moseley, Bohr, modern quantum mechanics etc. The role of the periodic table in the debate over the reduction of chemistry is discussed, including the attempts to derive the Madelung rule from first principles. Other current debates concern the concept of an "element" and its dual role as simple substance and elementary substance and the question of whether elements and groups of elements constitute natural kinds. The second of these issues bears on the question of further debates concerning the placement of certain elements like H, He, La and Ac in the periodic table.*

**Key words:** periodic table, history, philosophy, Mendeleev.

### Resumen

*El artículo muestra el estado actual de la investigación sobre las bases conceptuales de la tabla periódica. Damos una breve reseña histórica del desarrollo de la tabla periódica y el sistema periódico, en particular el impacto de la física moderna, debido a los descubrimientos de Moseley, Bohr, la mecánica cuántica moderna, etc. El papel de la tabla periódica en el debate sobre la reducción de la química se discute, incluso los intentos de derivar la regla de Madelung a partir de primeros principios. Otras discusiones refieren los debates actuales del concepto de un "elemento" y su doble función como sustancia simple y sustancia elemental y la cuestión de si los elementos y grupos de elementos constituyen tipos naturales. El segundo de estos asuntos tiene que ver con la cuestión de los debates sobre la posición de ciertos elementos como H, He, La y Ac en la tabla periódica.*

**Palabras clave:** tabla periódica, historia, filosofía, Mendeleev.

### INTRODUCTION

The periodic table of the elements is perhaps the most natural system of classification in the whole of science. Whereas biological classification is continually debated, the classification of the chemical elements is far more clear-cut as a result of the periodic table, although some disagreements still persist.

The periodic table is a physical representation of two more abstract notions, namely the periodic law and the periodic system, both of which are more fundamental than the familiar periodic table. Nevertheless, the terms periodic table and periodic system will be used somewhat interchangeably in what follows.

Unlike other sciences only chemistry possesses a single chart, the periodic table, which embodies the whole of the discipline both explicitly and implicitly given that new analogies and relationships continue to emerge from it. The periodic law, which underlies the periodic table, represents one of the big ideas in chemistry, along with the idea of chemical bonding, with which it is intimately connected. Not surprisingly, considerable attention has been devoted to the periodic table, and its fundamental aspects, in the philosophy of chemistry.

Before surveying the recent work that has been carried out it is necessary to briefly consider the historical evolution of this icon of chemistry as well as the forms in which it is commonly presented (SCERRI, 2007a). The idea of chemical periodicity is deceptively simple. If the elements are arranged in order of increasing atomic weight, as they were initially, approximate chemical similarities occur after various regular intervals. From this simple idea many far-reaching discoveries have followed concerning the structure of the atom, such as the manner in which electrons are arranged in shells around the nucleus. When discussing the putative reduction of the periodic table to modern physical theories, it is worth recalling that historically speaking it is the periodic table that led directly to many developments in modern physics. In a purely analytical approach to the philosophy of chemistry this fact may be less significant than in the historically informed approach that some authors adopt.

It has long been recognized that the periodic system does not fit into

the traditional categories which philosophers of science are accustomed to discussing. It is neither a theory, nor a model nor perhaps even a law of nature in the traditional sense. Yet the periodic system is capable of rationalizing vast amounts of information, and capable of making successful predictions. The philosopher DUDLEY SHAPER has provided an original analysis of the periodic system in which he concludes that it is rather an 'ordered domain' (SHAPER, 1977).

Not surprisingly, before the recent advent of philosophy of chemistry, philosophers of science devoted little attention to the periodic system, just as they neglected the whole of chemistry. There are some interesting exceptions, however. As long ago as 1958 KULTGEN produced a philosophical analysis of Mendeleev's ideas and the way in which he established his version of the periodic system (KULTGEN, 1958).

### A BRIEF HISTORY

From the early days when chemistry was just a qualitative science, chemists began to group together elements that were similar such as copper, silver and gold, the coinage metals. The beginnings of quantitative chemistry are not easily pin-pointed but they include the stoichiometric studies of LAVOISIER and RICHTER, followed by the establishment of laws of chemical combination and the Gay-Lussac law of combining gas volumes. Dalton's introduction of atomic weights provided a direct means of quantitatively comparing the various elements. For example, Döbereiner discovered the existence of various triads, that is groups of three elements such as lithium, sodium and potassium in which one element is intermediate in terms of chemical reactivity and also in its atomic weight. This finding pointed to an underlying numerical relationship that connects different elements to each other.

In 1860 an international congress held in Karlsruhe served to rationalize chemists' views on the meaning of 'atom' and 'molecule' and also led to a consistent set of atomic weights, the latter being due to CANNIZZARO. With this information in place, the stage was set for the independent discovery of the periodic system by six individuals, culminating in the work of LOTHAR MEYER and DIMITRI MENDELEEV in Germany and Russia respectively.

MENDELEEV receives most of the credit for not only producing the most mature and comprehensive periodic table but for also making predictions on the properties of elements that had not yet been discovered, three of which were amply verified over the following fifteen years. However, recent work in the history and philosophy of chemistry, and general philosophy of science, has reconsidered the extent to which successful predictions contributed to the acceptance of the periodic table by scientists of the time (BRUSH, 1996; SCERRI, WORRALL, 2001).

Several discoveries in physics of the early twentieth century had important consequences for the periodic table, although they have not changed it in any fundamental way. These discoveries include X-rays, radioactivity, the splitting of the atom, elemental transmutation, isotopy, atomic number as well as quantum mechanics and relativity. The discovery of atomic number by van den Broek and Moseley provided a more natural ordering principle than atomic weight which the pioneers had used. The new ordering principle resolved a number of 'pair reversals' such as in the case of tellurium and iodine which occur in the wrong order, in chemical terms, if one follows an order of increasing atomic weight.

Successive developments in atomic structure provided increasingly successful explanations of the periodic table in terms of electronic structure, although in many cases the periodic table led the way to discoveries in atomic structure rather than vice versa. Among these developments Bohr's model of the atom, one of the first applications of quantum theory to atomic structure, deserves special mention. In arriving at electronic configurations of atoms, which are then used to explain why certain elements are grouped together in the periodic table, Bohr approached the problem in a semi-empirical manner by appeal to chemical behavior and

spectral data. The Exclusion Principle which has far-reaching implications in all of science was motivated by Pauli's desire to explain the problem of the closing of electron-shells after their occupation by certain numbers of electrons. Although Pauli's approach of introducing a fourth quantum numbers, coupled with the previous work on the relationship between three quantum numbers, provided a fully deductive explanation for this phenomenon this was not the case for the more chemically important fact of the closing of periods. While the explanation of the closing of electron shells is frequently presented in science textbooks as the definitive explanation for the periodic system, the lack of a rigorous derivation of the point at which periods close stands in the way of a full reduction of the periodic system to quantum mechanics, as contemporary philosophers of chemistry have pointed out (SCERRI, 2007a).

The advent of a rigorous quantum mechanics in the period 1925-26 provided a more deductive approach to electronic configurations at least in principle. But not until methods of approximation had been devised by the likes of HARTREE and FOCK did it become possible to solve the Schrödinger equation for any particular atom to a reliable level of accuracy. From this time onwards the electronic configurations of atoms could be deduced in an ab initio manner, a claim that has been disputed by some philosophers of chemistry (Scerri, 2004) but defended by some theoretical chemists and physicists (SCHWARZ, 2007, 2009; OSTROVSKY, 2001; FREIDRICH, 2004).

**FORMS OF THE PERIODIC TABLE**

The original pioneer periodic tables generally consisted of eight columns to reflect the periodicity of the elements. These short form tables (figure 1) survived until well into the twentieth century. If elements are arranged in order of increasing atomic weight the approximate repetition in the properties of the elements occurs after eight elements until the element iron (atomic weight 55) is reached. To cope with this apparent break in periodicity Mendeleev was forced to remove sets of three elements such as iron, cobalt and nickel from each subsequent period and to place them into an anomalous group which he called the transition elements and labeled as group VIII.

Figure 1. Short-form periodic table.

MENDELÉEFF'S TABLE I.—1871.

Series.	GROUP I. R <sub>2</sub> O.	GROUP II. RO.	GROUP III. R <sub>2</sub> O <sub>3</sub> .	GROUP IV. RH <sub>4</sub> RO <sub>2</sub> .	GROUP V. RH <sub>5</sub> R <sub>2</sub> O <sub>5</sub> .	GROUP VI. RH <sub>6</sub> RO <sub>3</sub> .	GROUP VII. RH <sub>7</sub> R <sub>3</sub> O <sub>7</sub> .	GROUP VIII. RO <sub>4</sub> .
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	Ti=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	Y=88	Zr=90	Nb=94	Mo=96	—100	Ru=104, Rh=104 Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	? DI=138	? Ce=140	....	....	....	....
9	....	....	....	....	....	....	....	....
10	....	....	? Er=178	? La=180	Ta=182	W=184	....	Os=195, In=197 Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	....	....	....
12	....	....	....	Th=231	....	U=240	....	....

The next major change in the form of the periodic table occurred when sets of ten elements, rather than merely three, were removed

H																	He													
Li	Be											B	C	N	O	F	Ne													
Na	Mg											Al	Si	P	S	Cl	Ar													
K	Ca											Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
Rb	Sr											Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Figure 3. Long-form periodic table.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

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

Figure 2. Medium-long form periodic table.

from the main body of the eight column table, thus producing a block of thirty transition elements to which a further ten have been added more recently. The meaning of the term transition element also changed to denote an element whose atoms are in the process of filling inner, rather than outer, electron shells. The placement of these elements is typically made between the so-called s and p blocks or what constitutes the main-body of the former short-form table, and not on the right-hand side as Mendeleev had placed his transition elements. The reason for this placement is to preserve the order of increasing atomic weight, and later atomic number, in what is termed the medium-long form periodic table (figure 2).

Although not predicted, a new group belonging in the modern p-block of elements was discovered at the end of the nineteenth century. These elements are the noble gases helium, neon, argon, krypton, xenon and radon. The net result of this discovery is that although Mendeleev's group VIII became incorporated into the main body of the medium-long form table, a new group VIII emerged to take its place as far as the main-block elements are concerned. This means that the rule of eight of MENDELÉEV, ABEGG, KOSSELL and the octet rule of Lewis and Langmuir have persisted and continue to provide a simplified explanation for the occurrence of chemical bonding. Although there are many exceptions, there are also many cases in which elements form compounds in order to obey the rule of eight or, in modern terms, in order to achieve a full outer-shell of eight electrons (PALMER, 1965).

Even more recently, especially since new artificial elements were first synthesized in the 1940s, there has been a further change to the overall form of the periodic table. This change is somewhat analogous to the change from the short to the medium-long form in that the inner transition elements, formerly called the rare earths, have been removed to form the f-block, which is inserted between the s- and d-blocks, once again to preserve the order of increasing atomic number (figure 3) or often displayed as a footnote. The recent synthesis of elements up to and including element -118, with the exception of element 117, has led to speculation that the periodic table is due to undergo a further expansion to accommodate the g-block elements which will begin, at least formally, at element -121 (SCERRI, 2009b).



Finally, the synthesis of super heavy elements over the past 60 years or so, and in particular the synthesis of elements with atomic numbers beyond 103 has raised some new philosophical questions regarding the status of the periodic law. In these heavy elements relativistic effects contribute significantly to the extent that the periodic law may cease to hold. For example, chemical experiments on minute quantities of rutherfordium (104) and dubnium (105) indicate considerable differences in properties from those expected on the basis of the groups of the periodic table in which they occur. However, similar chemical experiments with seaborgium (106) and bohrium (107) have shown that the periodic law becomes valid again in that these elements show the behavior that is expected on the basis of the periodic table.

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