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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

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).

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.

MENDELÉEFF'S TABLE I.—1871.								
Series.	GROUP I. R ₂ O.	GROUP II. RO.	GROUP III. R ₂ O ₃ .	GROUP IV. RH ₄ , RO ₂ .	GROUP V. RH ₃ , R ₂ O ₅ .	GROUP VI. RH ₂ , RO ₃ .	GROUP VII. RH, R ₂ O ₇ .	GROUP VIII. RO ₄ .
I	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, Ce=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
II	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	
12	Th=231	...	U=240

H																
Li	Be															
Na	Mg															
K	Ca															
Rb	Sr															
Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
Fr	Ra	Ac	Th	Pa	U	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

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

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 MENDELEEV, 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).

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							

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The very concept of ‘elements’ that populate the periodic table is the subject on an on-going discussion dating back to the ancient Greek philosophers and their notions about the nature of matter. Is an element to be regarded as a fundamental abstract entity or a physically realized substance or perhaps as both? MENDELEEV, the discoverer of the periodic system had much to say on this question and held that the periodic table was primarily a classification of the abstract sense of the elements. There has also been a long-standing debate about how elements persist, if indeed they do, when present in compounds. Contemporary discussions in the philosophy of chemistry are largely based on a much cited paper by the radiochemist F.A. Paneth, who also suggested the current definition of a chemical element that was adopted by IUPAC in 1923 (PANETH, 2003). Paneth’s classic paper on the nature of elements was translated by his son, Heinz Paneth, who later changed his last name to Post. The terminology used by Post was ‘element as basic substance’ for Paneth’s Grundstoff and ‘element as simple substance’ for Paneth’s Einfacherstoff. This terminology and its interpretation has been the source of disagreement among contemporary authors (EARLEY, 2005; HENDRY, 2005; NEEDHAM, 2005; RUTHENBERG, 2009; SCERRI, 2009A; SHARLOW, 2006).

Given the interest in the question of the reduction of chemistry in contemporary philosophy of chemistry, the periodic table is playing at least two related roles in such studies. First it provides a more restricted domain upon which to focus the reduction question than 'the whole of chemistry'. Secondly, some authors have claimed that the periodic table does not completely reduce to quantum mechanics (SCERRI, 2004). Others dispute these anti-reductionist claims and emphasize that physics provides an approximate explanation of the periodic table (OSTROVSKY, 2005; SCHWARZ, 2007; FRIEDRICH, 2004).

For example, the structure of the modern periodic table is such that the length of successive periods repeat, with the exception of the very first short period of two elements. Some authors have claimed that this feature which is summarized in the Madelung, or $n + \ell$ rule of electron filling has not yet been deduced from quantum mechanics (LÖWDIN, 1969; SCERRI, 2004). More recently Schwarz has claimed that the Madelung rule is somewhat irrelevant since it refers to the ground state configuration of atoms in their unbound gas phase and not to atoms that have undergone chemical bonding (SCHWARZ, 2007). This brings us back to the question of how to interpret the term ‘element’ since Schwarz has also claimed that bonded atoms are equivalent to elements as basic substances, a view that has recently been challenged (SCERRI, 2009a). Quantum mechanics is by no means the only approach taken in trying to explain the periodic system from first principles. For example, Kais and Herschbach have tried to develop global approaches which promise to ‘solve’ the periodic table at one stroke instead of needing to solve the Schrödinger equation for each atom separately (KAIS et al., 1994).

been conducted. In 1985 the Dutch philosophers of science, Hettema and Kuipers, developed what they termed a ‘formalization’ of the periodic system, and used this as a basis to discuss the reduction of chemistry to atomic physics (HETTEMA, KUIPERS, 1988; SCERRI, 1997). LE POIDEVIN has referred extensively to the periodic table in a study claiming that chemistry does not even reduce to physics ontologically (LE POIDEVIN, 2005). Two independent criticisms of this article have appeared in the literature (HENDRY, NEEDHAM, 2007; SCERRI, 2007b). On the question of the law-like status of the periodic law, Christie has authored an article on the different ways in which chemists and philosophers regard the laws of nature (CHRISTIE, 1994).

A good deal of work exists on mathematical approaches to the periodic system using similarity studies (SNEATH, 2000; RESTREPO, PACHON, 2007), group theory (OSTROVSKY, NOVARRO, 1973), and information theory (BONCHEV, 2006). Some authors have begun to examine the philosophical significance of this work but much remains to be done (WANG, SCHWARZ, 2009; SCERRI, 2009c).

The perennial debate between realism and anti-realism (instrumentalism) has also been discussed in the context of the periodic system. For example some realists regard the elements as natural kinds and even that the elements in any particular group of the table might constitute a natural kind (HENDRY, 2009; SCERRI, 2005). It has also been argued that to be a realist about periodic system implies that such classification is an objective matter of fact and not a matter of convention, as some chemists often seem to claim (SCERRI, 2007a). This question bears strongly on the question of whether there exists an optimal form of the periodic table, even if such a table may not yet have come to light. As a matter of historical fact, over one thousand periodic tables have been published in print media alone and many more via the electronic media. What presumably motivates these variations is the intuition that an optimal form might indeed exist, a pursuit that is derided by some professional chemists. The latter response seems to reflect the belief that the periodic table rests on only its utilitarian value rather than its representing any form of ‘truth’ about the elements.

Of course there are many alternative tables that merely use a different shape, or a third dimension, to display the elements. Nevertheless, some variant tables do actually place traditionally troublesome elements like H, He, Al, Ac, La, Lu, Lr in different groups. Such debates among chemists and chemical educators have recently been enriched by more philosophical considerations on the representation of periodicity.

Among other more serious proposals for alternative forms of the periodic table are the pyramidal tables, which highlight so-called secondary periodicities, that were embodied in the original short-form tables. In addition the left-step table (fig. 4) as first proposed by CHARLES JANET in 1929, has been the subject of much discussion since it is said to reflect the quantum mechanical understanding of the periodic table to a greater extent than the conventional medium-long form table (BENT, WEINHOLD, 2007; SCERRI 2009a). A parallel discussion concerns the precise membership of group 3, an issue that raises many notions that lie at the heart of the modern periodic table such as the nature of electron configurations (LAVELLE, 2008, 2009; JENSEN, 2009. SCERRI, 2009d).

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The periodic system has served as the arena in which one of the most detailed attempts to reduce chemistry to atomic physics has

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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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