

ERIC R. SCERRI

EDITORIAL 8

SPECIAL ISSUE ON THE PERIODIC SYSTEM OF THE
ELEMENTS

The publication of this special issue is a special pleasure for me since I have been carrying out research on the periodic system of the elements for some years. Whereas many readers may have first become intrigued by chemistry after seeing some striking demonstration in their childhood, or by playing around with a chemistry set, others like myself may have been taken by the elegance and complexity of the periodic system. The periodic table is perhaps the most powerful icon of chemistry, because it seems to contain the whole subject within one single chart. Nobody who delights in classification and orderliness can fail to be struck by the beauty and the simplicity of the chemist's periodic system. Even people who have long ceased to study chemistry can usually dimly recall the periodic table from their school days, although everything else may have been forgotten.

I believe that the periodic system lies at the heart of philosophy of chemistry which, among other things, seeks to clarify the 'big picture' concerning the nature of chemistry. It seems rather obvious that if one is seeking an overall view of chemistry one should focus on that which provides the 'big picture' even within chemistry itself, namely the periodic system.

As is well known, the periodic system has matured and has been modified in specific ways over its 130-year history since the date of its 'official discovery' by Mendeleev in 1869. But it has also remained essentially unchanged in expressing the approximate repetition in the properties of the elements after certain regular but varying intervals have been crossed. The periodic system stands as a major challenge to the view that chemistry has been reduced to quantum mechanics. Indeed, it seems odd in some ways to think



of the periodic system as reducing to physics, since it has itself contributed to many discoveries in modern physics including the birth of quantum theory and quantum mechanics. Rather than being ‘explained away’ by quantum mechanics, as is sometimes implied, especially by contemporary chemistry textbooks, it is the periodic table itself that gave birth to the notion of electron shells and the Pauli exclusion principle, among other developments in theoretical physics.

I am thinking for example of the direct influence that the periodic system had on the scientific views of J.J. Thomson, who considered that an explanation of the periodic system was one of the most pressing problems for theoretical physics at the time. In his own work on the plumb pudding model of the atom, Thomson suggested that the electrons might circulate in specific rings which could each contain particular numbers of electrons. He proceeded to enumerate the world’s first electronic configurations which, though not entirely successful, provided the germ of the idea later picked up by Niels Bohr. Today electronic configurations are completely ubiquitous in chemistry and physics. Indeed, in chemical education they have become perhaps the most central paradigm. Rightly or wrongly, much effort is devoted to teaching chemistry students to write electronic configurations for any atom since it is believed that this one property, above all others, captures the chemical behavior of each element.¹

Niels Bohr’s classic trilogy paper of 1913, in which he introduced the quantum theory into the atomic domain, was motivated directly by the periodic system and a critique of the electronic arrangements and stability conditions which Thomson had published. It has more recently emerged that Bohr was not even aware of the hydrogen spectrum and its peculiar properties which he subsequently went on to explain, when he first began his work on the quantum theory of the atom. However, when he came to write the trilogy paper, which was intended primarily for an audience of physicists, Bohr began the article with his findings on the hydrogen spectrum and relegated the material on the periodic system to the lesser known third part of the article.

The Pauli exclusion principle, which is so far reaching in all areas of chemistry, physics, material science and even astrophysics,

was originally motivated by Pauli's desire to explain the problem of the 'closing' of the electron shells in 1924. But, although he may have provided a fully deductive explanation of the closing of the shells in terms of the relationships between the four quantum numbers, Pauli did not provide a similarly deductive explanation of the closing of the periods. It is of course the latter phenomenon which is of particular interest to chemists, whereas for all we know electron shells may not even exist. As some authors have claimed, it is by no means clear that quantum mechanics provides a deductive explanation of the periodic system, even in the light of contemporary *ab initio* calculations (Löwdin, 1969; Scerri, 1998).

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 1858 Kultgen produced a philosophical analysis of Mendeleev's ideas and the way in which he established his version of the periodic system (Kultgen, 1958). As with many great thinkers, like Einstein and Bohr, the work of Mendeleev confounds any simplistic attempts at pigeon-holing into the traditional philosophical categories like realism or anti-realism. The philosophical background of Mendeleev's work has been particularly neglected in this respect and there is much work to be done, particularly on the question of how he regarded the fundamental nature of the elements. Some preliminary steps in this direction have been taken most notably by Bernadette Bensaude (Bensaude, 1986; Scerri, 2000).

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. Yet the periodic system is capable of rationalizing vast amounts of information, and capable of making successful predictions. The philosopher Dudley Shapere has provided an original analysis of the periodic system in which he concludes that it is rather an 'ordered domain' (Shapere, 1977).

The periodic system has served as the arena in which one of the most detailed attempts to reduce chemistry to atomic physics has been conducted. In 1985 the Dutch philosopher of science Theo Kuipers, along with a colleague, Hinne Hettema, 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.²

More recently Maureen Christie produced a thought-provoking article on the different ways in which chemists and philosophers regard the laws of nature (Christie, 1994). This work included an analysis of the role of the periodic system, a theme which has been taken up more recently in a paper in which she was joined by her husband John Christie who is a theoretical chemist (Christie and Christie, 2000).

On the more historical side, there has been some renewed interest in Mendeleev's textbook, 'The Principles of Chemistry', which Mendeleev was in the process of writing when he arrived at the periodic system. It is natural to ask why Mendeleev failed to re-write his textbook in such a way as to place the periodic system at the center of his presentation. The traditional view has mainly been that Mendeleev preferred to add new information as footnotes in order to preserve the original form of the book and thus show the path which he took towards the discovery of chemical periodicity (Bensaude, 1984; Brock, 1992). The Japanese historian, Masanori Kaji, has recently challenged this view, although he has yet to publish his findings in any English language journal. Following an analysis of all successive Russian editions of 'The Principles of Chemistry', Kaji concludes against the more common view and claims that Mendeleev did in fact make substantial changes to his book following the discovery of the periodic system.³

Finally, before saying something about the articles in the present issue I would like to mention another area of scholarship in which the periodic system has been strongly implicated and which has enjoyed something of a revival in recent years. For as long as people have wondered about the nature of science there has been considerable disagreement over the relative merits of predictions and accommodations made by theories and which of these aspects, if any, should be considered to be more significant. The commonly held view, which is frequently illustrated by reference to the periodic system, is that successful predictions should be the chief criterion in the acceptance of a new scientific development. Several recent articles have appeared in an attempt to clarify this long-standing issue, and many of them have referred to the periodic system of

the elements (Maher, 1988; Lipton, 1990). Meanwhile, opponents of the view that predictions are more important than accommodations have highlighted examples from many areas of science to show that the successful accommodation of scientific data can sometimes be equally and perhaps even more significant in the course of theory change. One of these authors is the historian Stephen G. Brush (1989). But, somewhat curiously, Brush has been reluctant to accept that accommodation of already known data may have contributed as much or more to the acceptance of the periodic system by the scientific community than did Mendeleev's famous predictions (Brush, 1994, 1996). This in turn has provoked responses from those who do not believe that the predictions made by the periodic system were the over-riding reasons for its acceptance (Scerri and Worrall, in press).

PRESENT ISSUE

The first article in this special issue is by Carmen Giunta, a chemical educator who over the past few years has assembled a large collection of primary sources on a website devoted to the history of chemistry.⁴ In the present article he revisits an intriguing episode which lies at the heart of the evolution of the periodic system. When the first of the noble gases, argon, was discovered it was found to have a number of unusual properties which rendered its accommodation into the periodic system a particularly difficult problem. Unlike all the other elemental gases such as hydrogen, oxygen or nitrogen which are diatomic, argon appeared to be monoatomic according to considerations based on kinetic theory. In addition it was found to be completely unreactive, a fact that caused some chemists to suppose that it might not even belong in the periodic system of the elements. Furthermore, the atomic weight of argon relative to that of potassium presented one of the rare cases which would necessitate an atomic weight inversion in the periodic table, and which would not be fully understood until the discovery of isotopy some years later.

In the course of his article Giunta also discusses the question of the prediction of some other noble gases by Ramsey. This feature is of relevance to the recent philosophical debate concerning the

relative merits of predictions and accommodations in the acceptance of the periodic system by the scientific community. This is because the discovery of argon and its eventual accommodation into the periodic system has been taken to be somewhat influential in the retention, if not the initial acceptance, of the periodic system by some authors. Furthermore, as Giunta points out, the award of the Nobel prize to Ramsey was made not only for the discovery of the noble gases but for their placement into the periodic system.

The second article is by Helge Kragh, a leading historian of physics who has also made several forays into chemistry, especially in the context of Niels Bohr's early attempts to fix the electronic configurations of the elements in the periodic system.⁵ In the present article he revisits this territory but first reviews the earlier history of attempts to explain the periodic system in terms of models of the atom. It is now fairly well known that electronic configurations began with J.J. Thomson's electron rings, which contained specific numbers of electrons for each kind of atom. What is not so well known is that Thomson's views were directly descended from the earlier vortex theory of the atom introduced by Lord Kelvin in 1876. Kragh finds that the less successful early attempts to explain the periodic system by Thomson, Bohr and others were nevertheless highly regarded by chemists and physicists and thus finds support for the view by Lakatos that one should consider the long-term growth of research programs rather than individual theoretical contributions. Kragh concludes his article by addressing some issues arising from the earlier cited article by Shapere on the philosophical nature of chemical periodicity.

Valentin Ostrovsky is a theoretical physicist whose article in this issue has been partly motivated by recent work in the philosophy of chemistry and in particular some work on the periodic system. Ostrovsky addresses such questions as whether quantum mechanics has provided a deductive explanation of the periodic system and analyzes attempts made by physicists to deduce the order of filling of electron shells. He disputes the view that the *ab initio* calculations of properties such as ionization potentials of atoms represent genuine explanations since he likens such approaches to 'mathematical experiment'. As Ostrovsky points out, the computation of ionization potentials hardly contributes more to the understanding

of periodicity than the set of empirical data for the same property! Ostrovsky claims that his own mathematical analysis of chemical periodicity, using a corrected Thomas–Fermi model, provides an explanation for the Madelung, or $n + \ell$, rule for the filling of atomic orbitals. In addition he claims that this approach can cast light on the phenomenon of secondary periodicity which holds that alternate elements within any particular group of the periodic table show the greatest chemical similarities.

The issue closes with a bibliography of articles and books on the periodic system that I have compiled with the aid of Jacob Edwards, who is currently a promising undergraduate student at UCLA.

I think we can safely expect more philosophical studies on the periodic system in the years to come.⁶ It has become a commonplace in philosophy of science to emphasize that attention has largely shifted from theories to models or from a syntactic to a semantic analysis. The increased interest in the periodic system is clearly part of this trend, since it has been realized that to study chemistry demands that we study its models, or in this case its major organizing principle, rather than focusing on its allegedly deepest theories. The periodic system is more than the sum of its parts. It deals with phenomena all the way from macroscopically observable properties down to the structure of atoms and ions which are used to explain the same macroscopic chemical phenomena. There is no more striking or informative an icon anywhere in science as the periodic table of chemistry.

NOTES

1. But as chemical educator and historian Derek Davenport once remarked, students may know how to write the configuration of an element like chlorine but they often don't have the slightest idea of what its properties might be.
2. This article has come under a considerable amount of criticism (Scerri, 1997).
3. These views were presented orally at a History of Science session in Pittsburgh in 1999.
4. Giunta's web page containing classic papers in chemistry is at <http://webserver.lemoyne.edu/faculty/giunta/papers.html>
5. Although Kragh is willing to accept that Bohr's path to the electronic configurations of the elements was far from deductive, he seems to regard the prediction of the configuration and chemical nature of hafnium in a somewhat different light. See Kragh (2000), especially footnote 7, p. 444.

6. The present articles comprise the first part of a two-part special issue, the second of which will include contributions from chemical educator Henry Bent and historian of science Nathan Brooks among others.

REFERENCES

- B. Bensaude-Vincent, La Genèse du Tableau de Mendeleev. *Recherche* 159: 1206–1215, 1984.
- B. Bensaude-Vincent, Mendeleev's Periodic System of Chemical Elements. *British Journal for the History of Science* 19: 3–17, 1986.
- W.H. Brock, *The Fontana History of Chemistry*. Fontana, London, 1992.
- S.G. Brush, Prediction and Theory Evaluation *Science* 246: 1124–1129, 1989.
- S.G. Brush, Dynamics of Theory Change: The Role of Prediction. *Proceedings of the Philosophy of Science Association*, PSA 2: 133–145, 1994.
- S.G. Brush, The Reception of Mendeleev's Periodic Law in America and Britain. *Isis* 87: 595–628, 1996.
- M. Christie, Chemists versus Philosophers Regarding Laws of Nature. *Studies in History and Philosophy of Science* 25: 613–629, 1994.
- J. Christie and M. Christie, Laws and Theories in Chemistry Do Not Obey the Rules, in N. Bhushan and S. Rosenfeld (Eds.), *Of Minds and Molecules*. Oxford University Press, New York, NY, pp. 34–50, 2000.
- H. Kragh, Conceptual Changes in Chemistry: The Notion of a Chemical Element, ca. 1900–1925. *Studies in History and Philosophy of Modern Physics* 31: 435–450, 2000.
- J.H. Kultgen, Philosophic Conceptions in Mendeleev's Principles of Chemistry. *Philosophy of Science* 25: 177–183, 1958.
- P.-O. Löwdin, Some Comments on the Periodic System of the Elements. *International Journal of Quantum Chemistry Symposia* 3: 331–334, 1969.
- E. Scerri, Has the Periodic Table Been Successfully Axiomatized? *Erkenntnis* 47: 229–243, 1997.
- E. Scerri, How Good is the Quantum Mechanical Explanation of the Periodic Table? *Journal of Chemical Education* 75: 1384–1385, 1998.
- E. Scerri, Naïve Realism, Reduction and the 'Intermediate Position', in N. Bhushan and S. Rosenfeld (Eds.), *Of Minds and Molecules*. Oxford University Press, New York, NY, pp. 51–72, 2000.
- E. Scerri and J. Worrall, Prediction and the Periodic Table. To appear in *Studies in History and Philosophy of Science*.
- D. Shapere, Scientific Theories and their Domains, in F. Suppe (Ed.), *The Structure of Scientific Theories*. Illinois University Press, Urbana, IL, pp. 518–599, 1977.