Invited Article

The legacy of Mendeleev and his periodic system

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Received & Accepted: 18 September 2006
Published online: 30 September 2006

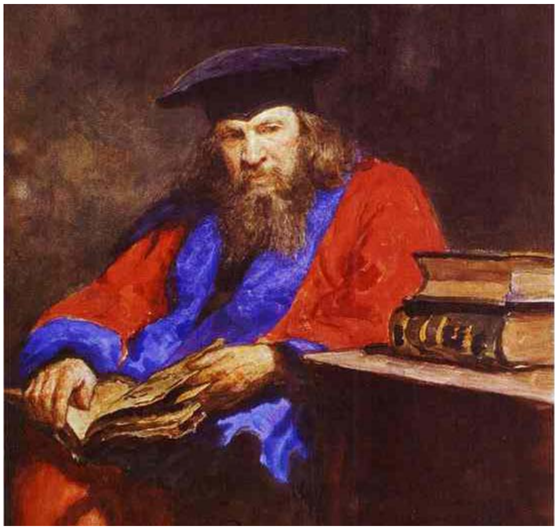
Next year is the one hundredth anniversary of the death of one of the most famous scientists of all time, the Russian chemist Dimitri Ivanovich Mendeleev (1834-1907). It is therefore appropriate to consider the lasting influence of Mendeleev and of his chef d'ouvre, the periodic system of the elements.

As is well known, Mendeleev was not the first to arrive at the periodic system although his version was the one that made the greatest impact in the scientific community. Before Mendeleev there were at least five scientists who produced some very respectable periodic systems, but were not able to capitalize too much upon their discoveries. The French geologist De Chancourtois obtained the very first periodic system, in fact a three dimensional system which he inscribed on the outer surface of a metal cylinder. Two English chemists Newlands and Odling, who coincidentally were born in the same London borough of Southwark, independently published periodic tables and both realized the need to reverse the positions of the elements tellurium and iodine. Just to back-track a little, the basic principle which all of these pioneers had realized, was that if the elements were ordered according to increasing atomic weight there would be an approximate repetition in their properties after certain well defined intervals. But there are a few stubborn exceptions to ordering the elements strictly according to atomic weight. Although the atomic weight of iodine is lower than that of tellurium, it was clear to Newlands, Odling and later Mendeleev, that the chemical properties of these elements required an exception to the ordering principle.

Another early system was due to the enigmatic, Danish born, Gustav Hinrichs whose path to discovery included some fanciful analogies with planetary astronomy and the newly discovered spectroscopic frequencies obtained from various elements. The closest precursor in chronological terms was the German chemist Lothar Meyer who arrived at a fully mature periodic system almost at the same time as Mendeleev. But a number of factors conspired to thwart Lothar Meyer's efforts including an untimely delay in the publication of his most elaborate periodic table. The usual account of the rivalry between Lothar Meyer and Mendeleev has it that only Mendeleev possessed the courage to make predictions on the properties of the elements that occupied empty spaces in his system. But this is an issue that even contemporary scholars of the periodic system continue to debate.

According to one school of thought, the successful accommodation of already known scientific facts is regarded as being equally important to successful predictions, in the acceptance of a new scientific development. This is despite the fact that predictions make a more dramatic impact especially on laypersons. But even if one were to discount Mendeleev's highly successful predictions of new elements it is clear that he also went a good deal further than Lothar Meyer in correcting the then known atomic weights of a number of elements such as uranium, titanium and beryllium.

And what about the lasting influence of Mendeleev's system? Needless to say the periodic system served to unify and organize the chemistry of the elements. No longer were students of chemistry obliged to memorize the properties of all the known elements. Henceforth they could learn the properties of at least one element from each column and could in principle make good predictions concerning the properties of other group members. More fundamentally perhaps, the eight-column table paved the way to G.N. Lewis' octet rule of chemical bonding and the notion of electron shells, some of which contain eight electrons. But I am getting ahead of the story.



Dimitri Mendeleev, Portrait by Ilya Repin

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Mendeleev, unlike some of his contemporaries, rejected any suggestion that the periodic system implied the existence of any form of primary matter of which all the elements were composed. He maintained that all the elements were strictly individual, indestructible and irreducible. But the evidence began to point in the opposite direction as Mendeleev was nearing the end of his life. Several revolutionary discoveries in physics began to show that the atoms of the various elements were reducible and that there was a deep sense in which all elements are indeed made of primary matter, namely electrons, protons and neutrons.

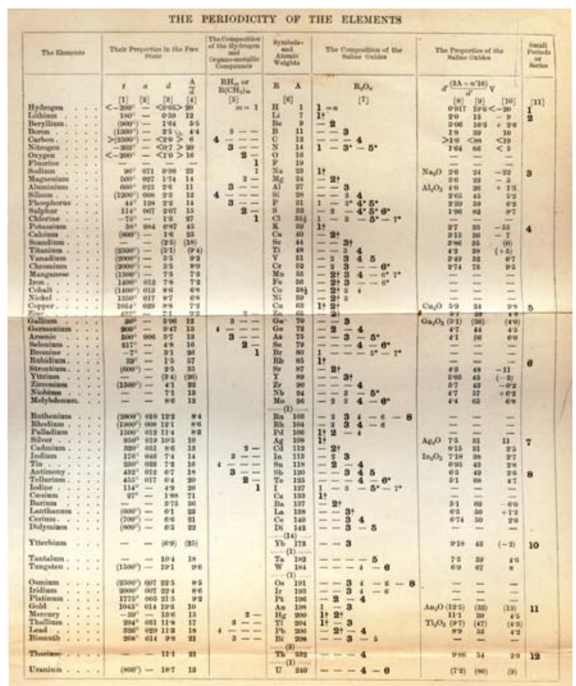
In 1879 J.J. Thomson in Cambridge discovered the electron, a particle that seemed to occur in the atoms of all elements. Shortly afterwards in Paris, the work of Becquerel, and especially the Curies, also implied that atoms of elements consisted of components that were coming apart in the course of radioactive decay. Thomson then attempted to explain the form of the periodic system by postulating the existence of rings of electrons embedded in the positive charge that comprised his plum pudding model of the atom. This was the origin of today's electronic configurations, which have become the explanatory paradigm in much of chemistry. The key to an atom's properties lies in the number of outer-shell electrons and that in turn is obtained by taking into account the configuration of all the electrons in the atom.

The origin of electronic configurations is most frequently and incorrectly attributed to Niels Bohr who introduced the quantum theory to the study of the atom. But Bohr was essentially tidying up Thomson's pre-quantum configurations and taking advantage of a more accurate knowledge of how many electrons each of the atoms actually possessed. Further developments in quantum theory, including Pauli's Exclusion Principle and Schrödinger's Equation, led to a more rigorous theoretical explanation of the form of the periodic system. Now it became clear why the first two periods contain two and eight elements respectively. The exact solution of the Schrödinger equation for the hydrogen atom reveals a set of characteristic quantum numbers. The manner in which these numbers are related to each other is rigorously constrained by the theory and the outcome is that the first two shells contain a maximum of two and eight electrons respectively. The build-up of successive elements, by the addition of a proton and an electron (and variable numbers of neutrons), produces period lengths of two and eight elements respectively. So far so good, but the third shell contains 18 electrons according to quantum mechanics and yet the third period in the modern periodic table contains eight and not 18 electrons.

If one takes into account the precise order in which electron shells and especially their sub-shells are filled this goes some way towards explaining the length of the third period, but the explanation is no longer neat and rigorous but is strictly semi-empirical. Here then is one essential aspect of the periodic system that continues to challenge the ingenuity of theorists and physicists to this day. Can a more fundamental solution be found that does not assume the experimentally observed order of sub-shell filling?

In addition there are some continuing debates concerning the best way in which to represent Mendeleev's periodic system. Should it be the original eight column short-form table, or the more contemporary eighteen column medium-long form or perhaps even a 32 column long-form table which more naturally accommodates the rare earth elements into the main body of the table? Alternatively some favor pyramidal tables while others prefer the left-step form originally proposed by Charles Janet in the 1920s. And very recently Philip Stewart of Oxford University has resuscitated a continuous spiral form of table.

Many chemists argue that the form of the table is of no importance but surely this is not so when rival forms position elements such as hydrogen and helium in quite different groups. Some philosophers of chemistry have argued that there may be an objective 'fact of the matter' regarding the kinship of helium for example. If this were so it would enable chemists to settle whether helium should be aligned with the noble gases or the alkaline earths, as it sometimes is on electronic grounds. And this is not a matter of convention as might be the choice between a pyramidal or a rectangular form of table.



One form of Mendeleev's periodic table, from the 1st English edition of his textbook (1891, based on the Russian 5th edition). [Image taken from www.wikipedia.org]

I would like to now turn to an area where Mendeleev's views have not been refuted but are indeed being re-examined in an attempt to clarify the philosophical foundations of chemistry. This topic concerns the distinction between elements regarded as basic substances as opposed to elements regarded as simple substances. The latter notion is by far the better known especially among chemists. Since Lavoisier all attention has been directed towards 'elements' in the sense of substances that can be isolated following the decomposition of compounds.

But there is a more abstract sense of the term 'element', namely a bearer of properties that cannot be isolated. It is carbon the basic substance that exists in all the isotopes of carbon or indeed in any of the allotropic forms of carbon. The fact that the element as a basic substance cannot be isolated has meant that its importance was relegated and perhaps even forgotten altogether especially since the rise of positivism in science. But Mendeleev did not ignore the distinction between simple substances and basic substances. More than most authors in modern chemistry, Mendeleev devoted considerable attention to elaborating the distinction. In many publications as well as subsequent editions of his Principles of Chemistry, he repeatedly emphasized that the periodic system was primarily a classification of elements as basic substances.

The distinction became rather important following the discovery of isotopes in the early years of the 20th century. Within a short period of time there suddenly seemed to be a profusion of 'atoms' or simplest possible substances to which all matter could be reduced. The periodic table, which was supposed to classify the simplest possible substances, was confronted with a major challenge. Some chemists including Fajans even called for an abandonment of Mendeleev's periodic system in favor of a more complicated table of isotopes. But other chemists, most notably Paneth, appealed to Mendeleev's distinction to argue that that the periodic table should remain as the focus of attention for chemistry, since what mattered more in chemical terms was the classification of elements as basic substances. All that the discovery of isotopes implied was an increase in the number of possible simple substances, or the less fundamental notion of elementhood.

Of course when really pushed even a contemporary chemist might admit the need for the concept of element as basic substance. For example one can ask a chemist about the substance that occupies the sixth place in the periodic system. What does it mean to refer to just an atom of carbon? Which of the particular isotopes would it be? The answer is that the sixth place in the periodic table does not refer to any particular isotope of carbon but the abstract notion of a carbon atom. Or in macroscopic terms what is the substance that belongs to the sixth place in the periodic table? Is it diamond, graphite or buckminsterfullerene? The answer is that it is none of these forms but whatever substance underlies these allotropes. It is carbon existing as the basic substance.

But whereas contemporary chemists adhere to an implicit notion of basic substances, if any, the growing community of philosophers of chemistry have recently devoted a good deal of attention towards clarifying the notion further since it is implicated in a number of perennial chemical questions such as the question of how, if at all, the elements survive following compound formation. Some of these philosophers hold that the notion of elements as simple substances is perfectly consistent with that of elements as basic substances and deny the lack of properties that is sometimes associated with them. Others believe that there is an irresolvable complementarity between the two notions and maintain, as Paneth did, that elements in the form of basic substances lack all properties with the possible exception of a few microscopic attributes such as atomic number.

To conclude, Mendeleev provided chemistry with its most profound organizing principle that even anticipates the discovery of quantum mechanics. The periodic system has also provided chemistry with its most potent icon, which is recognized by anyone with even a passing knowledge of chemistry. Even if students forget everything they ever learned, they tend to remember the existence of the periodic system. Moreover, the distinction between elements as basic substances and as simple substances, as stressed by Mendeleev, continues to exercise the minds of the current generation of historians and philosophers of science. For the discovery of the mature periodic system and for the clearest elaboration of the nature of elements we are indebted to Dimitri Ivanovich Mendeleev (1834 - 1907).

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