

## In the Year of Chemistry: From Mendeleev to Albert Einstein - The Periodic Table of the Elements and Beyond

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### About the Author

Peter Schwerdtfeger is the Director of the Centre for Theoretical Chemistry and Physics at the New Zealand Institute for Advanced Study in Massey University's Albany campus. He is a German and New Zealand citizen, having been born in Stuttgart in 1955 and gaining his education in that city with the University of Stuttgart his *almer mater*. His doctoral advisor was Heinz-Werner Preuss

Initially at the University of Auckland in the late 1980s, where he established a formidable reputation in theoretical chemistry and physics, Peter moved to Massey's Albany campus in its early days where he focuses on virtually all areas of electronic structure theory in chemistry and physics. He was awarded the prestigious Humboldt Prize, by the Alexander von Humboldt Foundation in Bonn (Germany) late last year for his fundamental work in the area theoretical chemistry and is a recipient of the RSNZ Hector Medal.

At 12, Peter was given a chemistry set and proved to be so good at blowing things up that his parents received a stern visit from the Stuttgart police. But his thrill of seeing what happens when one atom meets another is unchanged: *Science*, he says, *is fun*. The titles of his research projects lie in the polysyllabic jungle of *heterogeneous catalytic processes* and *electroweak interactions* but have connections to an extraordinary range of potential future technologies, from methods for finding new Alzheimer drugs to reducing the global warming effect of NZs burping cows, or even – one day – to ways to filter the methane out of gassy coal mines, reducing the chance of tragedies such as the Pike River Coal mine disaster.

Underpinning all of Peter's investigations is the grey area between physics and chemistry. He is expert at running extremely precise computer models of chemical reactions at the level of individual atoms, enlisting not only the quantum equations that describe the weird indeterminacy of the subatomic world, but also Einstein's relativistic equations that describe the weirdness of objects moving at high velocities.

Such high-speed relativistic effects are often disregarded by chemists, because the outermost electrons that cause atoms to cling together move pretty slowly. But, in fact, even small relativistic effects can be significant, and taking them into account has let him solve mysteries that some of us probably hadn't even realised were mysteries.

Members may remember that it was Peter and his Auckland team that organized the NZIC's 2006 conference in Rotorua.

**For me too, the periodic table was a passion. ... As a boy, I stood in front of the display for hours, thinking how wonderful it was that each of those metal foils and jars of gas had its own distinct personality** - Freeman Dyson, referring to the periodic table display in the Science Museum, London, which has element samples in bottles.

In 2008, the 63<sup>rd</sup> General Assembly of the UN has ratified a resolution (A/RES/63/209) proclaiming 2011 as the *International Year of Chemistry*.<sup>1</sup> The International Union

of Pure and Applied Chemistry (IUPAC) and the United Nations Educational, Scientific and Cultural Organization (UNESCO) strongly believe that *it is time to celebrate the achievements of chemistry and its contributions to the well being of humankind*.<sup>2</sup> No need to remind us that all living processes are controlled by chemical reactions, and that our understanding of the material nature in our universe and on earth is based on our deep knowledge of chemistry and its underlying physical principles, *viz.* that is relativistic quantum theory, thermodynamics, kinetics

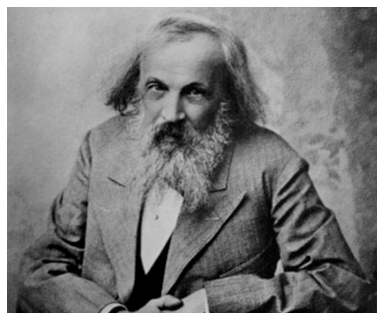


and electrodynamics. IUPAC plans to increase public appreciation of chemistry in meeting world needs, increase interest of our young people in chemistry, generate much needed enthusiasm for the creative future of chemistry, celebrate the 100<sup>th</sup> anniversary of the Nobel Prize recipient Madame Marie Sklodowska Curie, and the 100<sup>th</sup> anniversary of the founding of the International Association of Chemical Societies.

In such an eventful year we might reflect on what constitutes perhaps the most important development in the history of chemistry. This is not an easy task as many great discoveries come into our mind, all linked to outstanding chemists and brilliant minds (!), the true giants of chemistry on whose shoulders we all stand. Perhaps a look at the list of Nobel Prize winners over the last 100 years to discover some of the most influential achievements for which society would be poorer if these discoveries weren't made. Here I mention Emil Fischer's pioneering work on sugars and purines, Sir Ernest Rutherford's investigations into the atomic structure and the chemistry of radioactive substances, Marie Curie's discovery of the radioactive elements radium and polonium, Victor Grignard's discovery of the so-called Grignard reagent (which has greatly advanced the progress of organic chemistry), Alfred Werner's work on inorganic coordination chemistry, Fritz Haber's synthesis of ammonia from its elements (which is of immense value to our agricultural sector), Walther Nernst's development of thermochemistry, Irving Langmuir's discoveries and investigations in surface chemistry, Otto Hahn's discovery of the fission of heavy nuclei, Otto Diels and Kurt Alder's discovery and development of the Diels-Alder reaction, Hermann Staudinger's discoveries in the field of macromolecular chemistry, Linus Pauling's deep understanding and pioneering research into the nature of the chemical bond, Melvin Calvin's work on photosynthesis in plants, Karl Ziegler and Giulio Natta's development of high polymers (the Ziegler-Natta synthesis), Dorothy Hodgkin's structural investigations into insulin and vitamin B<sub>12</sub>, Robert S. Mulliken's fundamental work concerning the chemical bond and the electronic structure of molecules by using the molecular orbital method, Gerhard Herzberg's contributions to the knowledge of electronic structure and geometry of molecules, particularly the free radicals, Ernst Otto Fischer and Geoffrey Wilkinson's pioneering work on the chemistry of the organometallic (sandwich) compounds, Vladimir Prelog's research into the stereochemistry of organic molecules and reactions, Kenichi Fukui and Roald Hoffmann's theories concerning the course of chemical reactions, Herbert Hauptman and Jerome Karle's outstanding achievements in the development of direct methods for the determination of crystal structures, Henry Taube's work on the mechanisms of electron transfer reactions, especially in metal complexes, Dudley Herschbach, Yuan Lee and John Polanyi's contributions concerning the dynamics of chemical elementary processes, Paul Crutzen, Mario Molina and F. Sherwood Rowland's pioneering work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone, Alan Heeger, Alan MacDiarmid and Hideki Shirakawa's discovery and development of conductive polymers, Yves

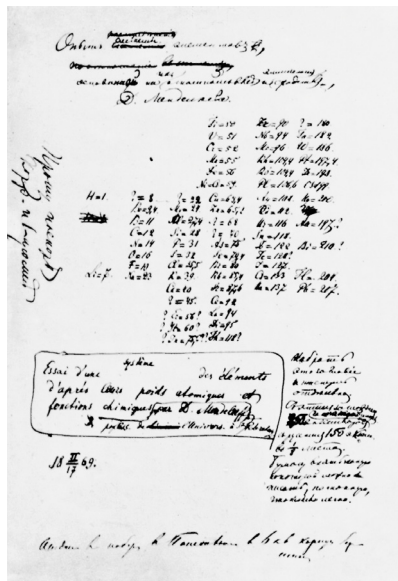
Chauvin, Robert Grubbs and Richard Schrock's development of the metathesis reaction in organic synthesis, and most recently Richard F. Heck, Ei-ichi Negishi and Akira Suzuki for the discovery of palladium-catalyzed cross couplings in organic synthesis.

So here we have the million-dollar question: which discovery has influenced our understanding of chemistry most? I argue that beside Dalton's early atomic theory interestingly termed *A New System of Chemical Philosophy* by him (!), and later work on atomic theory by Sir Ernest Rutherford, Erwin Schrödinger, Werner Heisenberg and Paul Adrien Maurice Dirac, it is Dmitri Ivanovich Mendeleev's discovery of the periodicity for the basic elements published in 1869 in *Zeitschrift für Chemie* (as there were no impact factors for journals at that time).<sup>3</sup>



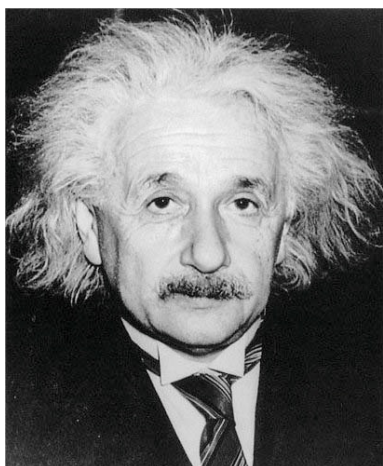
Dmitri Ivanovich Mendeleev (1834–1907)

Only one year later Julius Lothar Meyer independently announced the periodic system of elements (but Mendeleev came first and this is all that counts). Without the Periodic Table we would still be in the age of alchemy. And I guess there is not one chemist around in New Zealand who does not know the Periodic Table by heart (or at least one should hope so). For excellent historical accounts on the Periodic Table of elements see the excellent books written by Eric R. Scerri and Primo Levi.<sup>4,5</sup> Given this, the remainder of this article focuses on more recent developments concerning the extension of the Periodic Table into the superheavy element region.



Mendeleev's handwritten version of periodic system of the elements based on atomic weight and chemical resemblance (February 18, 1869)

In the years that followed Mendeleev's discovery, the distinct gaps for the then unknown elements he left were filled successively as chemists discovered new chemical elements. This continued through the last century until the last naturally occurring element proclaimed by Mendeleev was discovered in 1939 and named francium ( $^{223}\text{Fr}$ , a daughter nucleus of  $^{227}\text{Ac}$ , has a half-life of only 22 minutes). We all know that with the development of modern quantum theory by Erwin Schrödinger and Werner Heisenberg in the mid-1920s, and with the formulation of the exclusion principle by Wolfgang Pauli in 1925, each row (or *period*) in the Periodic Table corresponds to the filling of quantum shells (*s, p, d, f*) of electrons and to distinct electron configurations for the elements by using the so-called Aufbau (or building-up) principle as formulated first by Niels Bohr and Wolfgang Pauli. From the Janet-Madelung-Klechkowski (*n+l*) rule it follows that orbitals/states with lower *n+l* value are filled before the higher *n+l* ones. There are of course always exceptions to a rule as we all know, and for an excellent account on how quantum theory determines the position of an element in the Periodic Table, I recommend reading the recently published article by Shu-Guang Wang and W. H. Eugen Schwarz.<sup>6</sup>



Albert Einstein (1879–1955)

Before the development of quantum theory physics went through another important revolution – Albert Einstein's theory of relativity – long thought to be rather unimportant for understanding basic chemistry. Interestingly, the birth year of Albert Einstein coincides with Mendeleev's discovery of the Periodic Table. Another major development came with Paul Dirac's formulation of relativistic quantum theory in 1929 and I quote: *The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei.*<sup>7</sup> And then in 1988 Sheldon Lee Glashow wrote: *Modern elementary-particle physics is founded upon the two pil-*

*lars of quantum mechanics and relativity. I have made little mention of relativity so far because, while the atom is very much a quantum system, it is not very relativistic at all. Relativity becomes important only when velocities become comparable to the speed of light. Electrons in atoms move rather slowly, at a mere one percent of light speed. Thus it is that a satisfactory description of the atom can be obtained without Einstein's revolutionary theory.*<sup>8</sup> However, the understanding of the chemistry of the elements has changed substantially over the last three decades, as chemists slowly realized that Einstein's theory of relativity must not be neglected for the heavy elements. This is even more so the case for the newest entries in the Periodic Table, the trans-actinides, also known as the super-heavy elements that are generated synthetically and have limited lifetimes. In fact, the chemistry of the most recent extension of the Periodic Table is dominated by Einstein's theory of relativity, which Dirac could not foresee in 1929. Moreover, it is now well known and accepted that the chemistry of gold cannot be understood without the inclusion of relativistic effects. Pekka Pyykkö and Jean-Paul Desclaux pointed out in the mid-1970s that by using Dirac-Hartree-Fock calculations relativistic effects become more important in chemical bonding than originally presumed: *The orbital energies for non-relativistic AgH and AuH are quite similar while the relativistic ones are not. The non-relativistic bond lengths also agree within 3.0% while the experimental ones differ by 5.8%. This suggests that the chemical difference between silver and gold may mainly be a relativistic effect.* The unusual yellow colour of gold, the fact that mercury is the only metal that is a liquid at room temperature, the very small binding energy between thallium atoms (due to spin-orbit effects), and the unusual chain-like structures of gold halides in the solid state are prime examples for the importance of relativistic effects. The recent *gold-rush* in heterogeneous and homogeneous catalytic reactions involving gold as an efficient catalyst is also due to relativity.<sup>9</sup> Pekka Pyykkö wrote an excellent review article on the subject of relativistic quantum chemistry, which is also strongly recommended for reading.<sup>10</sup>

## Periodic Table of the Elements

IUPAC names

1	IUPAC names																18	
1s	H																He	
2s2p	Li	Be											B	C	N	O	F	Ne
3s3p	Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
4s3d4p	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5s4d5p	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6s5d6p	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7s6d7p	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	113	114	115	116	117	118
8s	119	120	5g7d8p9s9p...															
Lanthanides 4f	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Actinides 5f	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

The last naturally occurring element is Uranium with the atomic number of 92. The reason is that uranium has two isotopes  $^{235}\text{U}$  and  $^{238}\text{U}$  with rather large half-lives of 700 million years and 4.5 billion years, respectively. Heavier elements than uranium that were synthesized from neutron flux out of supernovae explosions have much smaller half-lives and were, therefore, long gone before the for-

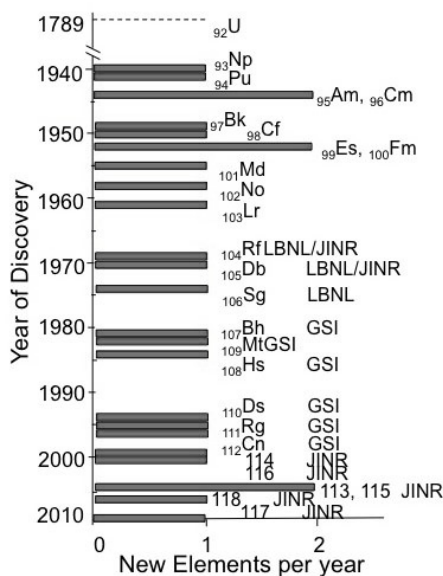
mation of our solar system, and so the search for trans-actinides (elements beyond nuclear charge 103, trans-fermium elements) remained fruitless. The newest additions to the Periodic Table, *i.e.* elements beyond the actinide series, are all synthesized artificially through nuclear fusion reactions that have very low production rates. It was Glenn Seaborg who pioneered the syntheses of the elements beyond uranium, and was the principal leader in the discovery of the elements from  $^{94}\text{Pu}$  to  $^{102}\text{No}$ , and for  $^{106}\text{Sg}$  named in his honour while he was still alive, a unique honour to a scientist. Isolation of a sizable quantity of any of the trans-actinide elements has never been achieved. By way of example, isotope 251 of Rutherfordium ( $^{251}\text{Rf}$ ) decays with a half-life of 78 seconds. For the super-heavy elements, the production rates are as low as one atom per week or month, and the synthesis of new elements requires radioactive beam facilities for neutron-rich beams and targets, to push the produced isotopes towards the predicted nuclear island of stability. The heaviest element for which atomic spectroscopy was applied to determine its atomic structure was  $^{255}\text{Fm}$  with a half-life of 20.1 hours. This isotope was produced at Oak Ridge laboratory (USA), where a sample of 1.7 ng was chemically extracted and air-shipped to Germany for experiments, and by the time that it arrived more than 95% of the  $^{255}\text{Fm}$  sample had decayed.<sup>11</sup>



Glenn T. Seaborg (1912–1999)

The newest elements that have entered the Periodic Table from 1990 onwards are Ds (Darmstadtium, 110), Rg (Roentgenium, 111) and Cn (Copernicium, 112) synthesized by the GSI Helmholtz centre in Darmstadt (Germany), and the elements with nuclear charge 113 to 118 were produced by the Joint Institute for Nuclear Research (JINR) group in Dubna (Russia) (see graph of discovery below) and are yet to be named. Chemistry on super-heavy elements can only be performed at a one-atom-at-time level, and is restricted to isotopes with half-lives of a few seconds or more. Such experiments have already been carried out for the elements up to Cn (except Mt, Ds and Rg, 109–111, respectively) in joint collaboration between the research groups at the Paul Scherrer Institute (PSI) in Villigen (Switzerland), the Society of Heavy Ion Research (GSI) in Darmstadt (Germany), the Lawrence

Berkeley National Laboratory in Berkeley (USA), and the Joint Institute for Nuclear Research (JINR) in Dubna (Russia), and preparations for atom-at-a-time chemistry on element 114 are currently in progress.<sup>12</sup> Chemistry for such short-lived isotopes are at the most extreme limit of chemical reactions, and needs to be supported by accurate relativistic quantum chemical calculations. For the future it is highly desirable to obtain more neutron enriched superheavy elements of near spherical nuclear shape close to the predicted nuclear island of stability in order to carry out atom-at-a-time chemistry with elements of much longer lifetimes. We currently do not know how we can achieve this ambitious goal.



A history of the discovery of the heavy and super-heavy elements; GSI: Heavy Ion research centre in Darmstadt; LBNL: Lawrence Berkeley National Laboratory; JINR: Joint Institute for Nuclear Research in Dubna

Recent quantum chemical calculations suggest that Cn is an element as small as Zn because of the strong relativistic  $7s$ -shell contraction, thus becoming inert to chemical reactions, and element 114 (eka-Pb) is predicted to adopt a closed shell configuration because of the large spin-orbit splitting of the  $7p$ -shell. Solid Cn is predicted to be a semiconductor with a small band-gap,<sup>13</sup> and element 114 is a solid metal similar to Pb with a rather low cohesive energy due to relativistic effects.<sup>14</sup> For an excellent account on super-heavy element chemistry and the importance of considering relativistic effects, the review article by Matthias Schädel is highly recommended.<sup>15</sup>

The placing of the new elements in the Periodic Table up to nuclear charge 120 is firmly accepted by relativistic quantum theoretical calculations. However, the correct placing of the elements from 121 onwards is less than clear-cut. The  $p$ -,  $d$ -,  $f$ -, and  $g$ -levels are lying so close energetically that a correct prediction for the ground state configuration becomes a formidable task. According to Shu-Guang Wang and Eugen Schwarz, this causes a complete breakdown of chemical systematics.<sup>6</sup> However, this has not hindered Pekka Pyykkö (Helsinki) recently to propose an extension of the Periodic Table including the elements up to nuclear charge 172, thus successively filling the  $8s$ ,  $5g$ ,  $8p$ ,  $6f$ ,  $9s$  and  $9p$  shells.<sup>16</sup> This newly ex-

tended Periodic Table will certainly cause a lot of discussion within our chemistry community. To verify Pyykkö's claims, accurate quantum chemical calculations including electron correlation and perhaps even quantum electrodynamic effects are required. And whether we will see the production of more super-heavy elements and exciting atom-at-a-time chemistry in near future, we just have to wait and see.

Glenn Seaborg was a well-known advocate of science education and of federal funding for pure research. However, over the last 20 years chemistry has been through a rather bumpy and long winding road with no end in sight - and that despite the fact that so many important recent discoveries were made. Let us all hope that 2011 brings some long-deserved awareness and necessary changes to foster and support chemistry research in our country. There is no quick solution to the many difficult environmental and financial problems human kind will face in not too distant future, but I am convinced that chemistry will contribute substantially to solving these problems. We need to get on with this sooner rather than later. For this we desperately need more Mendeleev's, Rutherford's, Seaborg's, MacDiarmid's and the like, and a better understanding by our administrations of how research really works, *i.e.* in mysterious and unpredictable ways, which makes chemistry such an exciting, creative and innovative subject.

#### Acknowledgments

I thank Brian Halton (Victoria University of Wellington) for suggesting I write this article. The pictures shown in the article

are freely downloadable from Wikipedia sites (copyright expired), and the Periodic Table created in our research centre is free for use as well.

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