Eka-francium *Et Seq.*

by Paul J. Karol

Ironically, the IUPAC Gold Book includes no definition of the "Periodic Table". Nevertheless, Chemistry International's readership assuredly knows what the Periodic Table is, or at least, what it has been, since that perception might change in the future. If the conversation is to be about prospects beyond the element with atomic number Z = 118, two essential questions must be answered: Where are we going? How will we get there?

The long-range growth of the Periodic Table, since the dozen or so "ancient elements", has sat at an effectively constant rate over the last two-and-a-half centuries, with a new element added every two-and-a-half years on average, although not necessarily sequentially. The evolution of the Table is illustrated in Fig. 1.

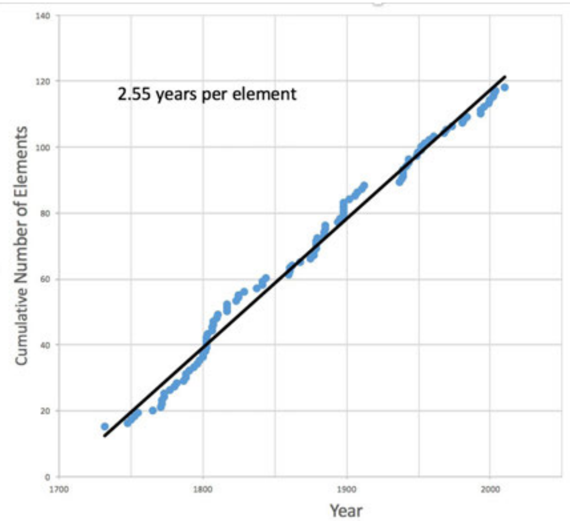

Fig. 1 Total number of known elements as a function of time expressed in calendar years.

Knowing where we are now, let us consider the two questions above. The first question has two aspects: nuclear structure and electronic structure. Without a nucleus, there is no element. A coarse characterization describing nuclear structure is embodied in the liquid drop model, now nearly three-quarters of a century old. The model, which we address only briefly, explains in a semi-quantitative way the broad behavior of nuclei: binding energies, fusion of light nuclei, most stable compositions, decay and reaction energies, fission energies and fissionability, shapes and barriers towards fission, and the location of particle "drip lines" at which compositions an additional proton or neutron will not "stick". The total binding energy reaches zero at about the mass number A = 3500. For heavy nuclei, a greater charge favors alpha decay and binary fission. Even ternary and quaternary fission can occur, as can the emission of clusters larger than alpha particles. Half-lives become shorter for higher Z. Fission becomes more probable with Z^2/A and inescapably instantaneous (in the liquid drop model) above $Z \approx 110$. But that Periodic Table cutoff was violated years ago. The nuclear shell model, conceptually similar to that for electronic levels in atoms, introduces extra stability at shell closures when merged into the bulk liquid drop behavior. For nuclear systems, both neutrons and protons can have closed shells, in which case nuclear scientists speak of "doubly magic" compositions. The stability associated with shell structure can be sufficient to overcome the high transition rates associated with both alpha-decay and fission and can also affect nuclear shapes and barriers. Seaborg seems to have been the first to reference the "island of stability" beyond the actinides. Exploration of the "island of stability" over the past years, with the anticipated nuclear stability, has focused on predictions of closed shells at Z = 114, 120, and 126, and also at N = 152, 162, 172, and 184. Newest to the Periodic Table are the *p*-block elements with atomic numbers 113 through 118, [1] whose properties strongly imply an island of stability has been reached (or breached) for those superheavy elements (SHE) where measurements show increasing, but still short lifetimes. SHEs are sometimes referred to as SHNs (superheavy nuclides), considered by chemists to be transactinides (Z > 103) and alternatively by physicists to have nuclear mass numbers A > 280.

Beyond the island (or cluster of islands) now being explored lies a vast ocean of instability that extends to a predicted, though distant, island of stability at Z = 164, perhaps the last in sight. Arguably, Z = 164 could be deemed the terminal edge of the Periodic Table. However, there are also calculations suggesting that changes in nuclear shape can profoundly affect this expectation. Both nuclear bubble and toroidal shapes suggest there may be "stable" compositions extending to Z = 240 and beyond. Nevertheless, Z = 164 is a huge extrapolation from the recently accessed island, fraught with the usual concerns about placing faith in such leaps. Current indications predict no stable (measureable) nuclides between that remote outlier and the nearer outcropping just being reconnoitered.

If there is a viable nucleus, what about the electrons? Electronic structure emerges from the wave behavior of electrons electrostatically attracted to a nucleus and repelled by other electrons. Relativistic considerations for atomic structure are exceptionally important: not only spin-orbit splitting, but other more esoteric effects emerge. For hydrogen-like (one electron) systems, we can look at the most tightly bound level, the *1s*. The Bohr equation gives a good account of its energy relative to the separated point-nucleus, point-electron arrangement, defining a zero and then including the rest mass energy of the electron itself, $m_e c^2$. The problem seems to have been first solved by Walther Gordon (of the Klein-Gordon relativistic Schrödinger wave equation) in 1928 [2]. The total energy, including rest mass energy, can be expressed in terms of the fine structure constant,

$$\alpha = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{\hbar c},$$

as $E_{1s} = m_e c^2 \sqrt{1 - Z^2\alpha^2}$, which gives unphysical results for $Z > 1/\alpha \approx 137$ and was identified early on as the upper limit for meaningful electron behavior, *i.e.*, a cutoff for the Periodic Table. Nearly four decades later, it was recognized that this obstacle could be circumvented if, rather than a point nucleus, a realistic finite size were considered. In this case, it turned out that the *1s* energy would continue to plunge deeper and deeper as *Z* grew beyond 137. But at a critical *Z* of about 172, the energy was sufficiently negative to allow a positron-electron (particle-antiparticle) pair to be created spontaneously out of the coulomb field in a vacuum, emitting the positron from the system and having the new electron occupy the "*1s*" level, forming a negatively charged vacuum in the nucleus' immediate environment [3]. This esoteric description is for the *1s* level initially unoccupied. But, of course, what is needed is recognition that the full ensemble of atomic electrons must be considered with whatever effects pertain to their mutual behavior. A many-electron treatment for argon gives essentially the same result for the behavior of the occupied *1s* level: a $Z_{critical}$ of about 172 [4]. This is basically the cutoff for any theoretical treatment of stable electronic configurations in a neutral superheavy atom, because there is no theoretical salvation beyond this point (yet). Arguably, it is the end of the Periodic Table or, at the least, of discussing the Periodic Table in contemporary language.

However, $Z_{critical}$ does not preclude a stable electronic environment at the distant island of stability for *Z* = 164. What happens in row eight and beyond, between the two islands? Attempts have been made to derive the appearance of an extended Periodic Table up to about *Z* = 170. The influence of relativity is manifest in several different ways. All the *s*- and *p*-electron radial distributions contract as illustrated in Fig. 2 in the case of calculations for eka-radium [4]. A consequence of the contraction of these orbitals and their influence on higher angular momentum orbitals is that the latter, the *d*- and *f*-orbitals, expand slightly. A third significant effect imposed by escalating relativistic considerations is the substantial increase in spin-orbit splitting. For example, the threefold degenerate *p*-states sever into a $p_{1/2}$ state and into a twofold degenerate $p_{3/2}$ state. How these developments are incorporated into projecting the Periodic Table into the 8th row and beyond will be briefly sketched out next.

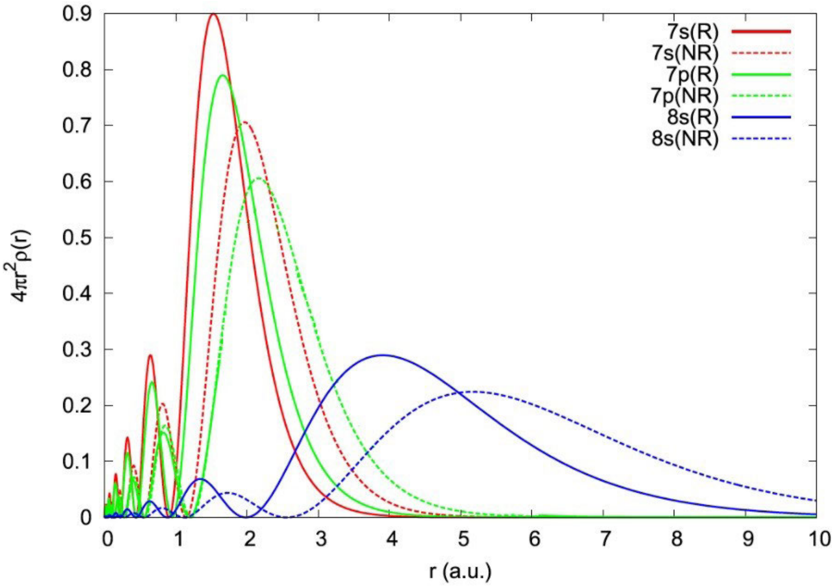

Fig. 2. For Z = 120, eka-radium, the radial density distribution functions for the 7s, 7p and 8s orbitals from the non-relativistic (dashed) and relativistic calculations. Adapted from [4].

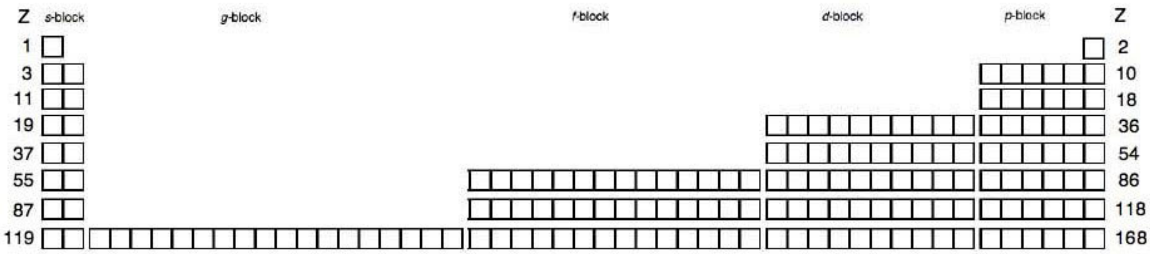

Fig. 3. Simplest extension of the Mendeleev-Seaborg contruct (see text for details)

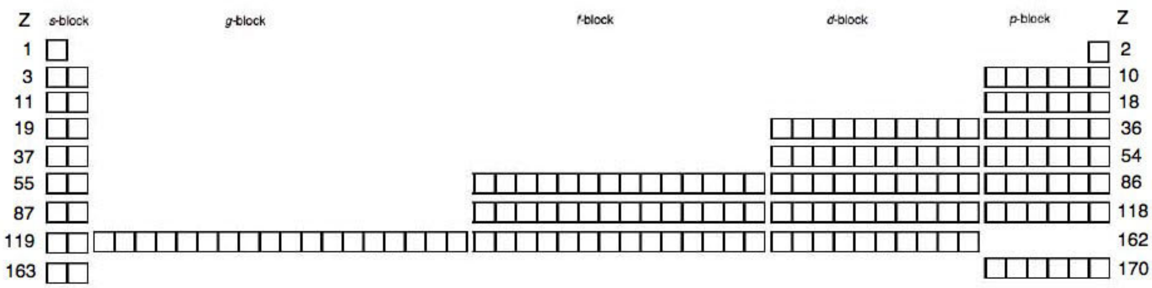

Fig. 4: Frickle et al [6] periodic table extension.

The first, and simplest, of these extensions is the *spdf* (*s*hell *p*artitioned *d*isplay *f*ormat) of the Mendeleev-Seaborg construction (Fig. 3), [5] which extends the Madelung (equal n+l) aufbau, having the 8th row begin with the *8s* level; followed by the *5g* block containing 18 "superactinides" or "octadecanoids"; in turn followed by, and sometimes combined with, the *6f* block with 14 members; then the *7d* with 10 and finally the *8p* with 6 elements, completing the 8th row at eka-oganesson, $Z = 168$.

In the Mendeleev-Seaborg Table, the element with atomic number $Z = 164$ emerges as a *p*-block element, suggestive of its possible chemical behavior. The anticipated first two elements in the 8th row, eka-francium and eka-radium, are *s*-block elements, and the next few, arguably within reach in the foreseeable future, are *g*-block elements. Significantly, for this Table and the alternatives to follow, even though the Table shows the *5g* filling after the *8s*, the electron configuration for the element with atomic number $Z = 121$ is predicted to be [Og] $8s^2 8p_{1/2}$.

Fricke *et al.* [6] constructed a different extended table, in which the element with atomic number $Z = 164$ emerges as an *s*-block element (in the 9th row). See Fig. 4. As with the Mendeleev-Seaborg picture, the first few elements in the 8th row show as *s*-block and *g*-block family members.

Fricke and Soff, in 1977, [7] further refined these predictions: for the first few 8th row superheavy elements, they envisage:

$Z = 121$ [Og] $8s^2 8p_{1/2}$
$Z = 122$ [Og] $8s^2 8p_{1/2} 7d_{3/2}$
$Z = 123$ [Og] $8s^2 8p_{1/2} 7d_{3/2} 6f_{5/2}$
$Z = 124$ [Og] $8s^2 8p_{1/2} 6f_{5/2}{}^3$
$Z = 125$ [Og] $8s^2 8p_{1/2} 6f_{5/2}{}^3 5g_{1/2}$

Most recently, Pyykkö [8] described a more strongly reconfigured Periodic Table, reproduced in Fig. 5. In this view, the element with atomic number $Z = 164$ projects as a *d*-block atom. The first several elements in the 8th row would follow the *s*-block, *g*-block sequence, based on ion configurations that Pyykkö evaluated. For atomic structures through $Z = 172$ ($\approx Z_{critical}$), the sequence electron configuration develops as $8s < 5g \leq 8p_{1/2} < 6f < 7d < 9s < 9p_{1/2} < 8p_{3/2}$.

Ordering the electron orbital energies is a prodigious task because of the critical imposition of relativistic considerations which themselves are not yet totally resolved *vis-à-vis* quantum mechanics. It is recognized that the various valence orbitals are not anticipated to be pure states but rather confounded by mixed configurations, what nuclear physicists alternatively call "mixed parentage". As an illustration, Nefedov [9] in 2006 considered the valence configuration of $Z = 125$. Eka-neptunium? Probably not. The preceding pictures suggest a configuration represented as [Og] $8s^2 5g^5$. Nefedov instead arrives at a mixed description that contains contributions from [Og] $8s^2 5g 6f^2 8p^2$ and [Og] $8s^2 5g 6f 7d^2 8p$ and [Og] $8s^2 6f^3 7d 8p$. Where do mixed configurations get placed on a Periodic Table that is founded on simple

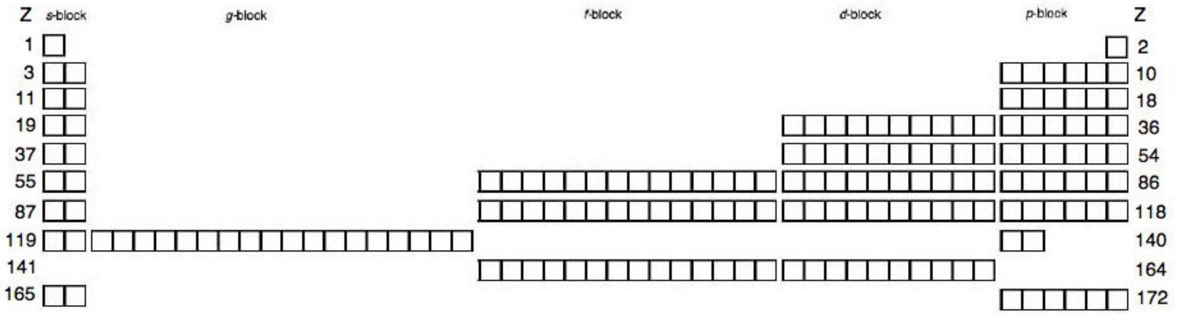

Fig. 5: Pyykkö [8] reconfigured periodic table.

electron configuration pedigree? That modest question is quite profound. But of course, if we don't get much beyond the next few new elements, it becomes moot.

Will new elements be produced? Accelerators used nowadays for superheavy element synthesis are cyclotrons or linear accelerators: the U400 at FLNR (Russia), the 88-Inch at LBNL (United States), the K-130 at JYFL (Finland), the UNILAC at GSI (Germany), the RILAC at RIKEN (Japan) or various cyclotrons at GANIL (France). The most successful methods for the synthesis of superheavy elements have been fusion followed by neutron evaporation reactions using heavy-element targets. Selective physical recoil-separation techniques of reaction products and the identification of nuclei, after implantation into position-sensitive detectors, are supplemented by seeking genetic ties to known daughter decay sequences. Fusion between Periodic Table row 7 elements serving as targets and ^{48}Ca beams are currently impractical beyond $_{118}$Og because long-lived targets above $_{98}$Cf, such as $_{99}$Es and $_{100}$Fm, are produced only with tremendous cost and effort. Einsteinium is available only in microgram quantities. 100-day ^{257}Fm availability is about a nanogram. To date, only a half-dozen attempts at row 8 have been made, none reporting convincing success (see Table 1). Increasing the number of neutrons in superheavy reaction products would increase their stability. But the production of isotopes with more neutrons requires fusion reactions with projectiles heavier than ^{48}Ca. Increasing the atomic number of the projectile also brings products closer to the stable proton shell(s) at Z = 120 and 126, where longer half-lives are expected. However, this will be a difficult undertaking. Most reaction models predict much lower cross sections for complete-fusion reactions with projectiles heavier than ^{48}Ca. For cold fusion and hot fusion, decreases by a factor of about 3.6 are evident for every increase in atomic number of the fused systems (see Fig. 6) [10]. However, predictions in the SHE quest have proven challenging, with uncertainties of one or more orders of magnitude in both yields and half-lives being the norm.

Target	*Projectile*	*Products*	*Year*	*Facility*
^{254}Es	^{48}Ca	$_{119}X_{183\text{-}x} + xn$	1985	Berkeley
^{244}Pu	^{58}Fe	$_{120}Y_{182\text{-}x} + xn$	2007	Dubna
^{238}U	^{64}Ni	$_{120}Y_{182\text{-}x} + xn$	2009	GSI
^{248}Cm	^{54}Cr	$_{120}Y_{182\text{-}x} + xn$	2011	GSI
^{249}Cf	^{50}Ti	$_{120}Y_{179\text{-}x} + xn$	2011	GSI
^{249}Bk	^{50}Ti	$_{119}X_{180\text{-}x} + xn$	2011	GSI

A dedicated facility is under construction: the "SHE Factory" at the Flerov Laboratory in Dubna, which will deliver significantly higher beam intensities than previously available. The French GANIL laboratory will soon open new facilities to study superheavies. The new Facility for Radioactive Ion Beams at Michigan State University will access new neutron-rich species. At GSI in Darmstadt, an accelerator with a beam intensity increased by a factor of 3.8 will serve to study superheavy nuclei. Anticipated improvements in target quantity, beam intensity, and transmission yield all bode well for the next handful of elements.

The possibility of multi-neutron transfer reactions using the heaviest feasible beams and targets has been considered as an alternative to the complete fusion synthesis route. Acceleration of beams of uranium are

Table 1: Reported attempts at raw 8. A number of additional experiments are scheduled for the immediate future. At Dubna, a mixed isotopic target $^{249, 250, 251}$Cf bombarded with ^{50}Ti is planned. At RIKEN, ^{248}Cm + ^{54}Cr will be pursued.

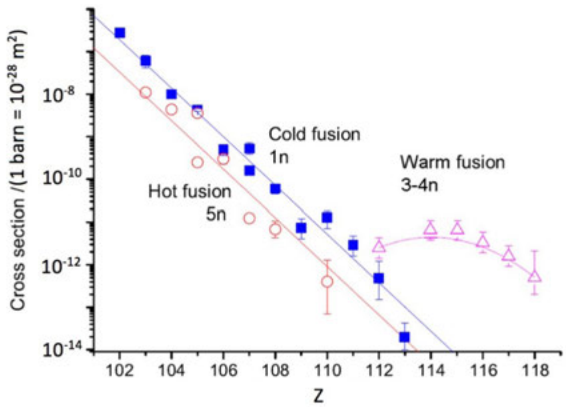

Fig. 6 Measured yields of superheavy elements grouped as evolving from high excitation energy compound nuclei (5 neutrons emitted), low excitation energy (1 neutron emitted) and "warm" excitation.

included in the designs at several accelerators. The possibility of surprising results from, for example, ^{238}U + ^{248}Cm or ^{136}Xe + ^{208}Pb are on the horizon, the former seemingly a potential channel to Z = 164.

On a final note, there is the intriguing possibility of identifying superheavy elements, including new ones, in nature. There are two possible sources. Supernovae explosions, occurring in our galaxy once or twice per century produce rapid, successive neutron captures that can furnish doubly magic, neutron-rich ^{78}Ni. During the explosive event, fusion with ^{208}Pb could generate an anticipated 50 teratonnes of (arguably) very long-lived darmstadtium. Also, recently discovered collisions between neutron star pairs and even black hole pairs might be spawning nuclei around A = 340 and stable N = 164, reactions taking milliseconds and expected to be more efficient than the supernova path, although definitely rarer. Reaction residues dispersed continuously throughout space could have materialized terrestrially at extreme trace levels, if at all.

Eponymous element hunters in Dubna, Yuri Oganessian on the left, then Georgii Flerov, and fifth is Glenn Seaborg.

Searches are underway, but appropriate chemistry is needed for their isolation.

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