

Some Comments on the Position of Lawrencium in the Periodic Table

William B. Jensen

*Department of Chemistry, University of Cincinnati
Cincinnati, OH 45221-0172*

A recent four-page, 23-author article in the 09 April 2015 issue of the journal *Nature* has reported an apparently successful experimental measurement of the first ionization energy of the short-lived radioactive element lawrencium (Lr) (1). First synthesized in 1961, Lr was initially assumed to have a $6d^17s^2$ valence configuration, analogous to the known $5d^16s^2$ valence configuration of its lighter lanthanoid analog lutetium (Lu), and both were assigned to the periodic table as the last members of the f-block, despite the fact that neither contained f-electrons in their outer valence configurations.

However, as early as 1971 it was suggested that Lr might instead have an anomalous $7s^27p^1$ valence configuration (2). This configuration is very close in energy to the idealized $6d^17s^2$ valence configuration and for years it was debatable which was the proper ground state for Lr – a debate that was all but ignored by most textbooks. It now appears that recent relativistic calculations have uniformly favored the $7s^27p^1$ choice and this is the configuration which the authors of the *Nature* paper accept. Indeed, they claim that their measured value of the first ionization energy of Lr, which is only 4.96 eV (478.9 kJ mol⁻¹) and numerically comparable to that of the alkali metals, is not only identical to the latest calculated theoretical value, but also in keeping with the relativistic configuration and the presence of an easily ionizable outer 7p-electron.

Implications for the Periodic Table

Beyond the above conclusions the authors of the *Nature* paper do not venture. They never doubt that Lu and Lr belong in the f-block nor do they confront the fact that the anomalous configuration of Lr would seem to imply – if one accepts the premise stated in their abstract that “the chemical properties of an element are primarily governed by the configuration of electrons in the valence shell” – that Lr should have the chemical properties of a Group 3 main-block element similar to thallium (Tl).

As chance would have it, the *Nature* paper was published almost simultaneously with a paper of my own (3) updating and defending an earlier 1982 paper

(4) in which I summarized chemical and physical evidence suggesting that Lu and Lr should be moved to the d-block beneath Sc and Y and that La and Ac, which had previously occupied that position, should instead be moved to the beginning of the f-block and treated as idealized $(n-2)f^1ns^2$ elements with anomalous $(n-1)d^1ns^2$ valence configurations, not unlike the case of Th, which has a $6d^27s^2$ valence configuration rather than the idealized $5f^27s^2$ configuration expected of an f-block element, but whose placement in the table has never been in doubt.

The person who linked my paper to the experimental paper was the reporter from *Nature* (5), who not only wished to do a news piece highlighting the forthcoming paper on the measurement of the ionization potential of Lr but to do so within the wider context of the debate over where Lr should be placed in the periodic table. And, with the exception of the coverage in *Chemical and Engineering News* (6), it was this broader question that has dominated all subsequent news stories on the *Nature* paper, as reflected in such suggestive titles as “Exotic Atom Struggles to Find Its Place in the Periodic Table” (5), “Lawrencium Experiment Could Shake Up the Periodic Table” (7), “Is the Periodic Table Wrong? Elements May Need to be Reordered After Scientists Find Lawrencium Looks Out of Place” (8), “Falsche Position in Periodensystem?” (9), and “New Data on Synthetic Elements Trigger Rethink of Periodic Table” (10).

When I wrote my first paper in 1982 all of the data I cited favoring the reclassification of the element pairs La/Ac and Lu/Lr involved a comparison of the properties of La versus Lu and of the group trends for the alternative choices Sc-Y-La versus Sc-Y-Lu with the corresponding group trends for the rest of the d-block for rows 4-6 (4). Since no data were available at the time for Lr or for elements 104-112 of period 7 of the d-block – most of which had not yet been synthesized – I relied on the basic premise of the periodic law that what was true of Lu was equally true of its heavier analog Lr.

As a result, I was initially taken off guard when various reporters began asking me point blank whether

	3+29	4+28	5+27	6+26	7+25	8+24	9+23	10+22	11+21	12+20	13+19	14+18	15+17	16+16
6	La 538.1	Ce 527.4	Pr 523.1	Nd 529.6	Pm 535.9	Sm 543.3	Eu 546.7	Gd 592.5	Tb 564.6	Dy 571.9	Ho 580.7	Er 588.7	Tm 596.7	Yb 603.4
7	Ac 499	Th 587	Pa 568	U 584	Np 597	Pu 585	Am 578.2	Cm 581	Bk 601	Cf 608	Es 619	Fm 627	Md 635	No 642

Figure 1. The values (in units of kJmol^{-1}) of the first ionization energy for the f-block elements as reported by Emsley (11). With the exception of the four elements highlighted in color, the ionization of the period 7 actinoid is always greater than that of the period 6 lanthanoid.

the newly reported ionization energy for Lr supported my argument concerning the reassignment of this element to the d-block. This caused me to look, as I had in my earlier paper, at the vertical trends in the first ionization energies for the other f-block elements using the values reported in the well-known handbook of element data by John Emsley (11) which quickly revealed that, with few exceptions, the value for the actinoid was greater than that for the corresponding lanthanoid, whereas the values reported in the *Nature* article for Lu and Lr were the exact reverse (522.8 versus 478.9 kJmol^{-1}). In addition, the value of the first ionization energy for both the lanthanoids and actinoids progressively increased *on average* (i.e. with the usual local ups and downs due to irregular configurations and half-filled subshells) on moving from left to right across the f-block (figure 1) – a trend that was radically at variance with the extremely low values reported for both Lu and Lr at the very end of the block. My comparison was mentioned by the reporter from *Nature* and was repeated in several of the subsequent news reports, where it was accompanied by various graphs to underscore the point.

Too late for inclusion in most of these reports was my further discovery that the measured ionization energies for Lu and Lr, though inconsistent with the idea that they were f-block elements, were totally consistent with the observed group trends for the first ionization

energies of the row 6 and 7 d-block elements (figure 2). My tardy recognition of this was due to my false belief that this data was unknown for elements 104–112 of row 7 and my subsequent surprise that values for these elements were in fact included in the handbook by Emsley, though I presume that they are all either theoretically calculated or empirically approximated.

In summary then, the experimentally reported first ionization energies of Lu and Lr are inconsistent with their assignment to the end of the f-block but totally consistent with their proposed reassignment to the d-block in the positions below Sc and Y.

The Problem of Electron Configurations

There is, however, a necessary caveat to this conclusion. Close examination of the reported ionization energies of La and Ac, given in figure 1, reveals that this pair of elements would work just as well as Lu and Lr in the positions below Sc and Y when it comes to vertical trends in the first ionization energies consistent with the other row 6 and 7 d-block elements. In other words, just as their identical maximum valence values of 3+ and their identical $(n-1)d^1ns^2$ valence electron configurations both fail to provide a definitive basis for deciding which pair of these elements should be placed below Sc and Y, the same is equally true when it comes

	3+15	4+14	5+13	6+12	7+11	8+10	9+9	10+8	11+7
6	Lu 522.8	Hf 642	Ta 761	W 770	Re 760	Os 840	Ir 880	Pt 870	Au 890
7	Lr 478.9	Rf (490)	Db (640)	Sg (730)	Bh (660)	Hs (750)	Mt (840)	Ds [955]	Rg [1023]

Figure 2. The values (in units of kJmol^{-1}) of the first ionization energy of the d-block elements of periods 6 and 7 as reported by Emsley. With the exception of the four elements highlighted in color, the ionization of the period 7 element is always less than that of the period 6 element.

to the vertical trends for their first ionization energies.

To tip the scales in favor of one pair of elements or the other requires instead a consideration of the additional chemical and physical properties discussed in my original paper of 1982 and, above all, a consideration of their available excited-state configurations (2, 4, 12). This reveals that both La and Ac have low-lying empty f-orbitals and that these are implicated in several low-lying excited configurations, whereas Lu and Lr have no available empty f-orbitals. This implies, in turn, that both La and Ac – like 25% of the other d- and f-block elements (including their nearest neighbor Th) – are best viewed as having anomalous ground-state valence configurations, which, in their case, take the place of an idealized $(n-2)f^1ns^2$ valence configuration. Since such an interpretation is not possible for Lu/Lr, it pretty much determines that this pair should be assigned to the d-block whereas the La/Ac pair should be assigned to the beginning of the f-block.

The same is equally true of the anomalous $7s^2p^1$ valence electron configuration for Lr, which lies only 0.18 eV below that of the idealized $6d^17s^2$ configuration. As already noted, a naive chemical interpretation of this configuration would suggest that Lr should have the properties of a Group 3 main-block element, such as Tl. However, there is no room for Lr in this group. The position beneath Tl is already assigned to element 113 and Lr is lacking the requisite $6d^{10}$ core. Measurement of the enthalpies of absorption and sublimation for Lr have also yielded values inconsistent with those of a typical p-block element and, despite its low first ionization energy, it has proved impossible to reduce Lr^{3+} to Lr^+ as might be anticipated by an analogy with the pair Tl^{3+}/Tl^+ (13).

All of this underscores the conclusion of my recent paper (3):

Though there are many misconceptions concerning the nature and function of the periodic law and table, perhaps the most prevalent among modern chemists is the belief that the periodic table is nothing more than an electron configuration table. While there is certainly a significant correlation between electron configurations and chemical periodicity, the correlation is, as already noted, far from perfect. The increasing prevalence of irregular configurations among the d- and f-block elements, the increasing lack of correlation between minor irregularities in these configurations and actual chemical behavior, and the ever present empirical question of how to properly divide an atom's configuration into the chemically relevant categories of valence versus core, all require a careful balancing of both chemical and physical evidence rather than an appeal to authority and a naive, and apparently arbitrary,

freshman chemistry application of spectroscopic atomic ground states.

Indeed, it also calls attention – in the case of anomalous configurations – to the necessity of looking not only at ground-state configurations but at available low-lying empty orbitals as well. This has led the author to recently propose, following the earlier work of Abegg, a set of group labels based on two, rather than one, number – one of which represents the total number of idealized valence electrons for the atom in question and the other of which represents the total number of idealized valence vacancies. This system not only resolves the placement problem for La/Ac versus Lu/Lr, but also for H and He and for the Zn group, as well as allowing one to rationalize the existence of primary, secondary, and tertiary relationships within the table and the various simplified bonding models taught in most introductory chemistry courses (14).

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