

Commentary I

The Positions of Lanthanum (Actinium) and Lutetium (Lawrencium) in the Periodic Table: An Update

William B. Jensen

*Department of Chemistry, University of Cincinnati
Cincinnati, OH 53706*

1. Introduction

Slightly more than 27 years ago I published an article in the *Journal of Chemical Education* entitled “The Positions of Lanthanum (Actinium) and Lutetium (Lawrencium) in the Periodic Table” in which I called attention to the fact that, based solely on their ground-state, outer $(n-1)d^1ns^2$ valence configurations, both La and Lu (and by implication their heavier analogs, Ac and Lr) had equal claim to placement in Group 3 of the d-block below Sc and Y (1). Since both La and Ac also had low-lying empty f-orbitals, whereas Lu and Lr did not, this fact alone strongly suggested that the former two elements had, like almost a quarter of the other d- and f-block elements, irregular configurations and should therefore be assigned to the first group of the f-block as idealized $(n-2)f^1ns^2$ elements, whereas Lu and Lr, for which this option did not exist, should be assigned instead to the first group of the d-block below Sc and Y.

To further support this conclusion, I compared groups trends in such properties as atomic radii, ionization energies, melting points, and electronegativity values for the alternative sequences Sc-Y-La versus Sc-Y-Lu with the corresponding group trends for the other members of the d-block and showed that the latter, rather the former, choice gave the best fit. Yet further evidence for this choice came from a comparison of the structures of metallic La versus metallic Lu with the structures of metallic Sc and Y, the structures of their oxides and chlorides, their superconductivities, the structures of their conduction bands, and their behavior during fractional crystallization. Once again all of these properties favored the placement of Lu rather than La (and by implication Lr rather than Ac) in the positions below Sc and Y in the periodic table.

Though over the years I have consistently used these conclusions in my subsequent publications on the periodic table, I never actively campaigned for their adoption by others nor aggressively attacked those who chose to ignore them. Consequently I was somewhat surprised on opening the November 2008 issue of the *Journal of Chemical Education* to discover a two-page commentary by one Laurence Lavelle entitled “Lan-

thanum (La) and Actinium (Ac) Should Remain in the d-Block” in which my initial 1982 paper was aggressively attacked as outdated, as well as an accompanying *Letter to the Editor* by the same author in which he claimed that he spoke “for the majority who are silent on this issue” for fear of being “attacked by the vocal proponents who insist that lanthanum and actinium must be in the f-block and lutetium and lawrencium must be in the d-block” (3). My initial surprise was two-fold: surprise that the *Journal of Chemical Education* had given me no warning that this attack was about to appear nor an opportunity to reply as part of the initial commentary, and surprise that an active army of militant proponents, including apparently myself, were aggressively engaged in suppressing all attempts to resist such a reassignment of La and Ac in the periodic table. But my greatest surprise came on reading the commentary itself and discovering the inconsistent reasoning and misleading distortions used by Lavelle to support his claims.

2. The Placement of Lutetium

While initially admitting that the comparative group property trends supporting the reassignment of Lu to the d-block were - at least at first glance - “reasonable,” Lavelle immediately turned around and attacked the relevance of such evidence using the time honored technique of first setting up a nonexistent straw man (2):

However, many elements with similar properties or similar trends in properties are not placed in the same group. For example, the well known diagonal relationships as found in lithium (Li) and magnesium (Mg), beryllium (Be) and aluminum (Al), and boron (B) and silicon (Si) would, applying the same reasoning, result in lithium (Li) and (Mg) in the same group because they have similar physical and chemical properties. For example their respective atomic radii are 1.57 Å and 1.60 Å and both react directly with nitrogen to form nitrides. Similarly for boron (B) and silicon (Si), which are metalloids, with electronegativities of 2.0 and 1.9 respectively (Pauling scale). Why not place

them in the same group? Indeed, why not place all the metalloids in the same group as they have similar properties?

and then attacking it (2):

The answer is a resounding no. As the above examples illustrate, similarity (or trends) of properties is not the de facto standard for placing the elements in the same group. The placing of elements in the periodic table is currently accepted as a combination and balance of factors including the empirical observations: atomic number, properties, periodic trends, and atomic ground-state electron configurations.

In actual fact, when assigning an element to a position in the periodic table the above factors are not simply applied as a haphazard empirical blend or combination, rather they are applied in a strictly hierarchical order, consisting of four steps or stages (4):

1. Assignment the element to a major block based on the kinds of available valence electrons (i.e., s, p, d, f, etc.)
2. Assignment of the element within a given block to a particular group based on the total number of available valence electrons.
3. Verification of the validity of the resulting block and group assignments through the establishment of consistent patterns in overall block, group and period property trends.
4. Verification that the elements are arranged in order of increasing atomic number as required by the periodic law.

Only when criteria 1 and 2 fail to lead to an unambiguous group assignment does one resort to the application of criterion 3. This was, of course, precisely the case with the question of whether La or Lu should be placed in Group 3 below Sc and Y and was the reason why I had to resort to the use of self-consistent group property trends. Never, with the possible exception of an unfortunate article by Cronyn, also published in the *Journal of Chemical Education* (5), has the matching of properties other than valence been taken, historically or otherwise, as the primary standard for assigning elements to groups in the periodic table.

So why, if Lavelle was aware of this, did he consume so much space in first suggesting and then attacking nonsensical group assignments based property-matching between nonisovalent elements randomly

selected from different rows and columns, none of which would have gotten beyond step 2 of the above hierarchy, if not to mislead readers of the *Journal of Chemical Education* into thinking that I had applied the “same faulty reasoning” in my original paper and so underhandedly discredit, in lieu of any proper scientific arguments, the evidence favoring the placement of Lu in the d-block?

Indeed, in a more recent exchange of *Letters to the Editor* entitled “Misapplying the Periodic Law,” in which I accused him of having knowingly done just that when he attempted to satirize my use of self-consistent group trends by equating them with “the arbitrary pairing of elements randomly selected from different rows and columns in the hope that a fortuitous cancelation of trends will lead to property matching,” he rather disingenuously dismissed the charge as “incomprehensible” and as an attempt on my part to gain attention through the use of a “catchy” but otherwise “incorrect” title (4, 6)

In the above exchange Lavelle also complained that proponents of the assignment of lutetium and lawrencium to the d-block “are selective in the literature they cite to support their claim,” though this is precisely what he did himself in his initial diatribe, since not only did he attempt to misrepresent the use of group trends through misdirection, he also failed to inform the readers of the *Journal* that much of the literature that has appeared on this subject in the 27 years since I published the initial paper has in fact tended to support the proposed reassignment of Lu.

Thus in a 2000 paper in the *Journal of Chemical Physics* on the spectroscopy of Lu₂ dimers in argon matrices, Lombard *et al.* concluded (7):

The lower value for the Lu₂ force constant measured here fits the trends for the other rows and columns [of the d-block] better than that from La₂ ... In addition to Jensen's arguments, we would like to add the observations of the relativistic corrections to the contraction of the 6s shell from the calculations of Desclaux. A plot of the ratio of the relativistic (r_{6s}) to the nonrelativistic value is shown in [figure 1]. Note the sharp break in slope between Yb and Lu. At least relativistically Lu belongs to the d-block elements and the lanthanides should run from La through Yb. This combined with our measurements of dimer force constants adds weight to the arguments in favor of reexamining the common placement of La and Lu in the periodic table.

Likewise in a 2008 article in the same journal by Feng *et al.* on a first principle computational study of AIX (X = 3d, 4d, 5d and Lu) dimers, the authors concluded (8):

The present calculations show that the triplet state ($^3\Sigma^-$) is the ground state for AlSc, AlY and AlLu, while the quintet state ($^5\Sigma^-$) is the ground state for AlLa. This discrepancy suggests that AlLa has a different chemical bond compared with its congeners AlSc, AlY and AlLu. This discrepancy raises the question as to whether it would be more suitable to replace La with Lu in the periodic table.

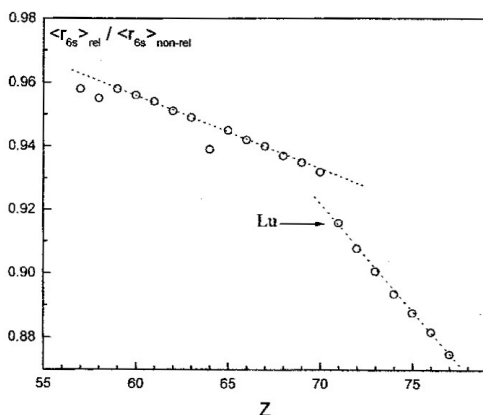


Figure 1. A plot from reference 7 of the ratio of the relativistic to the nonrelativistic radii for the 6s orbital versus Z for La and the lanthanoids ($Z = 57-70$) and for the row 6 d-block elements through Ir ($Z = 71-77$) which clearly shows that Lu belongs to the d-block trend and La to the lanthanoid trend.

3. The Placement of Lawrencium

Throughout his initial diatribe Lavelle repeatedly emphasized that all of the empirical evidence cited by me for the placement of Lu and Lr in the d-block actually involved Lu and was only *assumed* to apply to Lr as well. This is true, since, at the time, none of the necessary property values used in the group trends were available for either the highly transient Lr atom, or for the largely missing heavier, row 7 analogs of the d-block, and the same is equally true today. This is, of course, why both lawrencium and actinium appeared in parentheses in the original title. In making the assumption that what was true for La and Lu was equally true for both Ac and Lr, I was simply applying the primary postulate of the periodic law.

The assumption that Lr had a $6d^17s^2$ valence configuration analogous to the $5d^16s^2$ valence configuration of Lu was first made by Mellor in 1970 and is still assumed by all major inorganic textbooks and monographs on the periodic law. But, as Lavelle was quick to point out in his initial attack, more recent calculations have suggested that the actual ground-state valence configuration of Lr is instead $7s^27p^1$, thus predicting that its properties and “compounds are more like Tl.” Lavelle professed great surprise that I was

ignorant of this “news” and, since the first speculations on this alternative configuration supposedly go back to the work of Brewer in 1971 (9), and thus predate my paper, this forms the basis of his charge that I and other proponents of placing Lr in the d-block have been selective in our citation of the literature. In fact, I never came across any references to this claim when reviewing the literature in 1980 (recall there is usually a two-year delay between submission and actual publication in the *Journal of Chemical Education*) and, as already noted, it had little subsequent impact on either the inorganic textbook literature or the literature on the periodic table. Indeed, Brewer provided no explicit discussion of this prediction and it was instead tucked away in one of the 31 tables that appear in the paper. Consequently it comes as no surprise that it was also not highlighted in any of the various summaries and abstracts of the paper.

Moreover, Lavelle failed to inform the readers of the *Journal* of the various qualifications voiced in the three literature references which he which initially cited in support of this claim (10-12). Thus the paper by Haire has virtually no explicit discussion of the implications of this newer valence configuration and merely lists it in a table, along with the earlier $6d^17s^2$ configuration, where it is qualified by brackets and a question mark (11). The detailed discussion by Silva, on the other hand, is far more specific, noting that earlier calculations showed that “the energy difference between these two configurations [i.e., $6d^17s^2$ versus $7s^27p^1$] was quite small and either configuration could be the ground state,” and that, while more recent calculations have uniformly favored the $7s^27p^1$ alternative, this prediction has in fact failed one of the few attempts to experimentally test the resulting implication that Lr and its compounds should have properties similar to those of typical p-block metals, such as Tl or Pb, rather than those of typical d-block metals, such as Sc, Y and Lu (12):

In 1988 Eichler and coworkers proposed gas adsorption chromatography experiments to distinguish between the two ground state configurations s^2d and s^2p . They calculated that there should be a measurable difference in the enthalpies of adsorption on metal surfaces for the two different configurations ... The s^2p was predicted to be [more] volatile, perhaps similar to the p-element Pb, than the s^2d configuration with estimated sublimation energies of 134 and 400 kJ mol⁻¹, respectively. Online gas chromatography was applied to study the volatility of Lr by Jost et al. (1988) and to determine the enthalpy of adsorption. No evidence for Lr as a volatile element was found under reducing conditions at a temperature of about 1000°C. Their

results gave a lower limit for the adsorption enthalpy for Lr on quartz and Pt surfaces at 290 kJ mol^{-1} , significantly higher than the estimated values for Lr (s^2p^1). The configuration of the ground state of lawrencium is still in doubt.

Ironically, these experimental results actually appeared graphically in the paper by Haire, reproduced below as figures 2 and 3, though he provided no discussion of their significance relative to the question of the proper ground-state configuration for Lr.

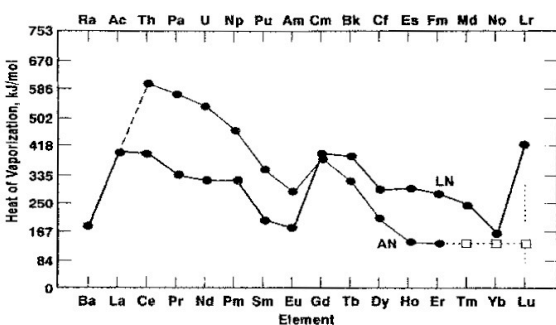


Figure 2. A plot of the enthalpy of vaporization versus Z for both the lanthanoids (LN) and actinoids (AN) taken from reference 11. Note the strong deviation of Lu relative to the overall trend for La-Yb and the failure of Lr (open box) to parallel this deviation based on predictions of an assumed $7s^2 7p^1$ valence configuration versus its actual experimental behavior (vertical dotted line) which does. The plot is somewhat confusing as the two sequences cross at Gd/Cm.

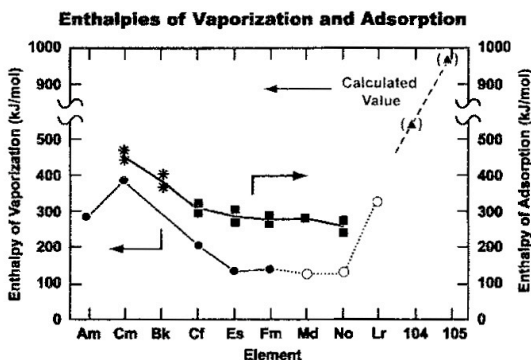


Figure 3. Plots of the enthalpy of vaporization and the enthalpy of adsorption of the actinoids taken from reference 11, showing the strong deviations for Lr consistent with its interpretation as a d-block, rather than an f- or p-block element.

It is also worth noting in passing that figure 2 actually provides additional evidence for the placement of Lu in the d-block and La in the f-block beyond that cited in my original paper. This is confirmed by the trends in the enthalpy of vaporization for the alternative group sequences Sc-Y-La versus Sc-Y-Lu, for which the latter, rather than the former, corresponds

most closely to the group trends observed for this property for the other elements in the early part of the d-block.

As with Lavelle's failure to cite the recent literature supporting the reassignment of Lu to the d-block and his use of misdirection to discredit the use of periodic trends, his suppression of the actual conclusions of Silva concerning the controversy over the ground state configuration of Lr calls into serious question the way in which he has selectively employed his references in an attempt to support his preconceived notion that La and Ac must, at all costs, remain in the d-block. Even if experiment should eventually confirm the predicted $7s^2 7p^1$ configuration for Lr, it is certain that one cannot consistently argue, as Lavelle does, that this result would absolutely negate all arguments for placing Lr in the d-block as a heavier analogy of Sc, Y, and Lu, but would have absolutely no bearing on the question of whether it should remain in the f-block.

The most plausible interpretation of an experimental spectroscopic confirmation of the predicted $7s^2 7p^1$ configuration would be that Lr is just another example of a d-block element with an irregular (albeit unique) configuration which still functions chemically as an analog of Lu rather than as a typical p-block element. Such a disjunction between the spectroscopic configuration of an element and its chemical behavior is hardly unique. As Jørgensen pointed out many years ago, the correlation between the electron configuration of an isolated atom and its chemical behavior is not always very precise (13):

There is not the slightest doubt that no simple relation exists between the electron configuration of the ground state of the neutral atom and the chemistry of the element under consideration. Thus iron and ruthenium differ much more from each other chemically than do nickel, palladium, and platinum, though the configurations are analogous in the former case but differ in the latter. The most spectacular discrepancy between the spectroscopic and chemical versions of the periodic table is that helium is an alkaline earth element from the standpoint of spectroscopy, since its configuration does not terminate with np^6 like the other noble gases. Hence, it is not too surprising that the almost invariant trivalency of the lanthanum series has little to do with the ground states of the neutral atoms.

In other words, the experimental data of Jost *et al.*, as described above by Silva, may ultimately have little bearing on the question of whether Lr does or does not have a $7s^2 7p^1$ configuration, though they are of great importance in confirming that Lr continues to function as a chemical analog of Lu rather than as an analog of

Tl and would thus follow Lu in its proposed reassignment to the d-block.

4. The Placement of Lanthanum and Actinium

When it comes to the question of why La and Ac should remain in the d-block rather than being reassigned to the f-block, Lavelle offers no new chemical or physical evidence other than his constant reiteration of the fact that both elements contain d-electrons in their ground-state valence configurations, but no f-electrons. Yet in the cases of both Lu and Th, for which this is equally true, he proceeds to inconsistently argue that this fact is of no consequence when it comes assigning them to the f-block. As with the case of the revised configuration for Lr, which counts when it comes to not placing this element in the d-block but is irrelevant when it comes to placing it the f-block, this arbitrary and naive use of electron configurations, to the exclusion of all other evidence, is logically inconsistent and leaves one with the impression that the only true argument that Lavelle has for the major premise of his diatribe is that La and Ac should remain in the d-block because that is where IUPAC places them in its official periodic table and therefore all rational discussion of other possibilities is strictly forbidden.

5. Summary and Conclusions

In summary, Lavelle provides no substantive scientific evidence for why Lu should not be reassigned to the d-block based on both its ground-state valence-electron configuration, the absence of any low-lying, readily accessible f-orbitals, and self-consistent groups trends for various chemical and physical properties. Instead he attempts to side step this issue through misdirection and failure to cite the current literature supporting this reassignment. Likewise he provides no new positive chemical or physical evidence for why La and Ac should not be reassigned to the f-block or for why Lr, despite its newly calculated configuration, should not continue to be regarded as a chemical analog of Lu. Instead, he ignores the evidence for irregular configurations and the loose correlation between these configurations and chemical behavior and instead relies solely on their ground-state valence configurations coupled with apparently arbitrary criteria for when they are or are not of significance when it comes to assigning the elements in question to either the d- or the f-blocks.

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.

Regrettably this absence of positive scientific evidence, whether pro or con, has become even more apparent in the recent exchange of *Letters to the Editor* (4, 6), in which Lavelle again applies misdirection by consuming considerable space in answering the question of why his original commentary was written, in refuting the charge that it was merely unreviewed personal opinion, in disproving the claim that there is substantial historical precedent for placing La and Ac in the f-block, and in defending IUPAC, Herb Kaesz and Peter Atkins. The only problem is that in my initial letter, to which his was ostensibly an answer, I never asked the first question, never leveled the second charge, never made the third claim, and never voiced the fourth criticism. Indeed, in all of my publications on the periodic table I have repeatedly pointed out that, prior to the late 1940s, the current f-block elements were all placed, along with La, in what is now the d-block, where they were either dispersed among the various groups or treated as degenerate members of Group III (14). Nowhere does Lavelle respond to my explicit question as to what criteria he uses, when assigning elements to the f-block, for deciding when an element's valence-electron configuration is irrelevant (Th, Lu, Lr) and when it is absolutely prohibitive (La and Ac). And, sadly, in his final paragraph, he adds the further fallacy of the *ad hominem* attack to his arsenal of evasive tactics.

6. References and Notes

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