209. On the Misleading Interpretation of the Properties of the *f*-Electron Elements

by **Irena Fidelis**

Department of Radiochemistry
Institute of Nuclear Research, Warszawa

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Summary

The aim of the paper is to elucidate the problem of the regular changes in the properties of *f*-elements represented by the double-double effect. It is pointed out that because of the half-filled shell and double-double effects the *f*-element properties cannot be plotted as a linear function of the L-quantum number, as suggested by *Sinha* [1] [2].

Sinha reviews the various lanthanide properties and correlates them in terms of the 'inclined W' plots [1] [2]. This constitutes however a misleading interpretation of the existing experimental data.

Any consideration of the validity of the idea of 'inclined W' plots, should take into account (1) the half-filled shell effect [3], and (2) the double-double effect discovered in form of the 'regularities' in the separation factors or in stability constants [4]. The former effect, first demonstrated experimentally by *Seaborg*'s group [5] using ion exchange chromatography, is based on the observation that the f^6- and f^7-electron elements are more similar to each other than those with the f^7- and f^8-electron configurations.

The main feature of the double-double effect is the analogy between the f^0-f^7 and f^7-f^{14} subgroups, each of which can be further divided into 2 segments, and the analogy between the differences observed within the 4 segments: f^0-f^3, f^4-f^7, f^7-f^{10} and f^{11}-f^{14}, the differences between neighbouring elements within each segment decreasing with the number of *f*-electrons *(Fig. 1)*.

No symmetry, however, is observed when the differences between adjacent elements are concerned. Such a symmetry with respect to the f^7 configuration and to the central pairs f^3-f^4 and f^{10}-f^{11}, is required by the 'inclined W' plot hypothesis [1].

A plot of the experimentally observed changes in properties of *f*-elements as a function of the L-quantum number is presented in *Figure 2*. This shows a linear correlation in case of the first (f^0-f^3) and third (f^7-f^{10}) segment, which may occur because just for these 2 segments the differences between consecutive L-numbers, S, F, H, I ($L = 0, 3, 5, 6$ and $\Delta L = 3, 2, 1$) decrease with Z which, by chance, correlates with the decrease experimentally observed for each of 4 segments *(Fig. 1)*. However, in order to follow the pattern of 'inclined W' plot, the differences within the second (f^4-f^7) and fourth (f^{11}-f^{14}) segment should increase with Z, because the differences

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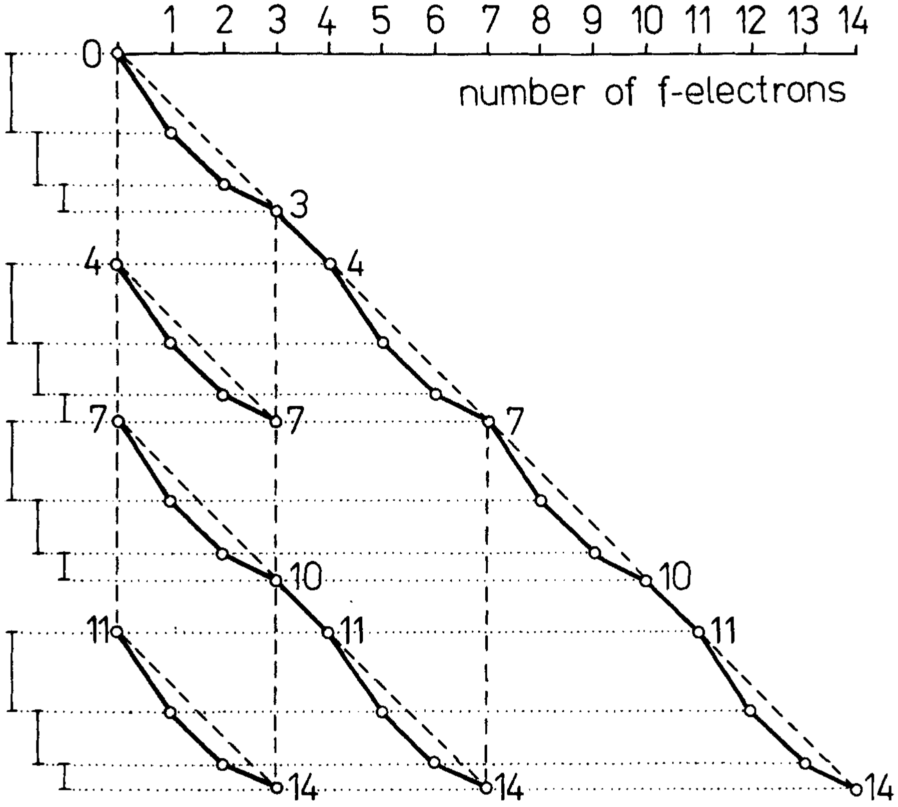

Fig. 1. *Schematic pattern of changes in properties of* f-*elements plotted as a function of Z.* Double-double effect; the analogy between the 2 subgroups: f^0-f^7 and f^7-f^{14}, and between the 4 segments: f^0-f^3, f^4-f^7, f^7-f^{10}, f^{11}-f^{14}.

between the respective L numbers, I = 6, H = 5, F = 3 and S = 0 (ΔL = 1, 2 and 3, respectively) increase with Z, while experimentally the reversed order is observed (the small differences for the Eu(III)-Gd(III), Am(III)-Cm(III), and Yb(III)-Lu(III) pairs are particularly well known).

Although the *f*-element properties cannot be plotted as a linear function of the L-quantum number, as suggested by *Sinha*, another kind of correlation between the *f*-element properties and the sequence of L-quantum numbers does exist [6]. This correlation consists in the existence of the double symmetry within both the sequence of the L-values, and the sequence of the relative stability of the *f*-electron configurations, *i.e.* the double-double effect.

In connection with *Sinha*'s work [1] [2] one should emphasize that to interpret the extensive experimental material, it is necessary to apply a statistical approach rather than draw somewhat arbitrary straight lines. Such a statistical approach has been applied by *Siekierski* to most of the experimental data on stability constants of various lanthanide and actinide complexes [7], and lattice parameters of numerous lanthanide [8] and actinide compounds [9]. The general validity of the double-double effect has been established that way.

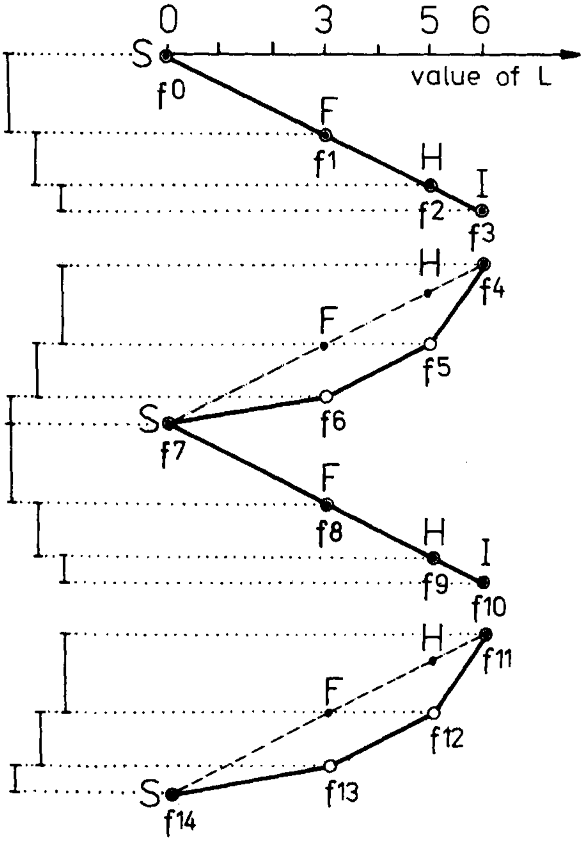

Fig. 2. *Schematic pattern of changes in properties of* f*-elements plotted according to* Sinha, *as a function of the* L*-quantum number.* Open circles denote the schematic pattern according to the double-double effect, and full points - according to 'inclined W' hypothesis.

In connection with *Nag*'s work [10] one should emphasize that the separation factors determined from the chromatographic data [4] are much more reliable than the static extraction coefficients, and their ratios. Thus, the variation of the separation factor as a function of the lanthanide pair plotted on the basis of chromatographic data is more accurate than plots of the relative extraction coefficients or stability constants against the atomic number, based on the static extraction data.

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