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Periodicity and the Lanthanides and Actinides

Periodicity is defined as the tendency to recur at regular intervals. As applied to the chemical elements, the term indicates the regular recurrence of particular types of chemical and/or physical properties as a function of some atomic parameter such as ground-state electronic configuration or nuclear charge. In discussing periodicity as it relates to the lanthanides and actinides, or more generally to the *f*-type transition elements, we are concerned, therefore, with systematizing recurrent characteristics.

The *f*-type transition elements present problems that are somewhat different from those encountered with other types of elements as consequences both of the general shielding of *f* orbitals by higher-level orbitals and of the inherent differences in shielding experienced by the 4*f* and 5*f* orbitals. These problems render reasonable a discussion under the somewhat separated headings

1) Periodicity in relationship to the other elements
2) Periodicity between the lanthanide and actinide series
3) Periodicity within each series

Periodicity in Relationship to the Other Elements

The original Mendeleev table of 1869, as reproduced in Table 1, listed, of the elements in question, only Er, Ce, La, Di, Th, and Ur. The element Yt, which is not an *f*-transition element but which as a consequence of charge-size similarities is operationally included to advantage with the lanthanides, also appeared in this table. Prior to 1869, only the elements La, Ce, Th, Ur,

and Yt had been truly characterized as pure substances (*1*). The Di of Mendeleev's table was not resolved into Pr and Nd until 1885. The Er listed was undoubtedly the mixture *erbia*, the resolution of which was not effected until many years later.

The positions assigned in 1869 by Mendeleev bear little relationship to those we now recognize. In part, this situation resulted from inaccuracies in atomic weight data produced by errors in combining weights. In part, it resulted also from lack of purity in samples available for study and thus an incomplete knowledge of correct chemical properties.

The Mendeleev table of 1872, as reproduced in Table 2, listed no additional elements from the series in question but did achieve a better correlation of properties, as we now know them, by placing Yt, Di, and Er together in Group III, Th in Group IV, and U in Group VI and basing this classification on a more nearly correct assignment of atomic weights. The inclusion of Ce in Group IV was undoubtedly based upon the better characterization of the +4 oxidation state of this element, but the assignment of La to this group was probably more the result of yet another error in atomic weight.

Subsequent modifications of the Mendeleev table included other lanthanides as they were separated and characterized but could, in terms of their restrictive geometries, do little more than suggest that the lanthanides are an unclassifiable group of elements which, in terms of their very similar properties, occupy only a single position in Group III following barium in Group II. Indeed, even the problem of the total number of elements that can be in this series had no answer until the theoretical considerations of N. Bohr set the

Table 1. Mendeleev's Periodic Table of 1869

I	II	III	IV	V	VI
			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	T = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104.4	Pt = 197.4
			Fe = 56	Ru = 104.4	Ir = 198
			Ni = Co = 59	Pd = 106.6	Os = 199
H = 1			Cu = 53.4	Ag = 108	Hg = 200
	Be = 9.4	Mg = 24	Zn = 65.2	Cd = 112	
	B = 11	Al = 27.4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210
	O = 16	S = 32	Se = 79.4	·Te = 128	
	F = 19	Cl = 35.5	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85.4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87.6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75.6	Th = 118?		

Table 2. Mendeleev's Periodic Table of 1872

Series	Group R₂O	Group II RO	Group III R₂O₃	Group IV RH₄ RO₂	Group V RH₃ R₂O₅	Group VI RH₂ RO₃	Group VII RH R₂O₇	Group VIII RO₄	
1	H = 1								
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19		
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5		
4	K = 39	Ca = 40	= 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Ni = 59	Co = 59, Cu = 63
5	(Cu = 63)	Zn = 65	= 68	= 72	As = 75	Se = 78	Br = 80		
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	= 100	Ru = 104, Pd = 106	Rh = 104, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127		
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140					
9									
10			?Er = 178	?La = 180	Ta = 182	W = 184		Os = 195, Pt = 198	Ir = 197, Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208				
12				Th = 231		U = 240			

upper limit at nuclear charge $(Z) = 71$ (2). These considerations and their subsequent extension to the preferential and essentially sequential occupancy of the $4f$ orbitals as being responsible for both the existence of and the similarities in properties among the lanthanides provided the rationale for the logical inclusion of these elements in a suitably modified form of the periodic table.

Earlier theoretical and semitheoretical postulations as to the existence of a second f-type transition series were verified by both a reexamination of the naturally occurring elements Ac–U and an evaluation of the synthetically produced transuranium species (3). Electronically, of course, the elements in the series Ac–Lr $(Z = 89-103)$, i.e., the actinides, proved to be exact or nearly exact analogs of the lanthanides.

Except for the inevitable geometrical problems imposed by the necessity of crowding, the modern extended tabulations based upon ground-state electronic configurations of the atoms accommodate both the lanthanides and the actinides without problems and show their periodic relationships to the other elements. The table proposed by Seaborg (4), and included here as Figure 1, does this quite clearly and in addition indicates similar periodic relationships based upon yet undiscovered elements of the $6f$ type. In the majority of these tabulations, lanthanum and actinium are included as direct electronic analogs and congeners of scandium and yttrium. The lanthanides are then the elements Ce–Lu, inclusive; the actinides Th–Lr, inclusive. However, propertywise, and thus operationally, lanthanum and actinium may be considered in these categories. It is apparent, of course, that the lanthanides provide a bridge between the elements of Groups IIA and IVB. The actinides should then do likewise, with Element 104 being a congener of hafnium.

Extended forms of the periodic table, such as that shown in Figure 1, have the advantage of pointing out clearly the electronically separate classes of elements and relating each class to the other. Thus the lanthanides and actinides are clearly members of transition series within d-transition series, or of inner transition series (5). As such, their atoms and ions may be expected to show certain parallels in properties to those of the d species, but differences that reflect the more extensive shielding of the f orbitals. In the sense that these elements follow directly those in Group IIA, their atoms and ions may be expected also to reflect trends in properties noted in the sequence Group IA–Group IIA. Both of these expectations have abundant experimental support. It is unnecessary in this brief summation to delineate in any more detail periodic relationships to other elements.

Periodicity between the Lanthanide and Actinide Series

Periodicity between the two series should be a consequence of recurring electronic configurations of the
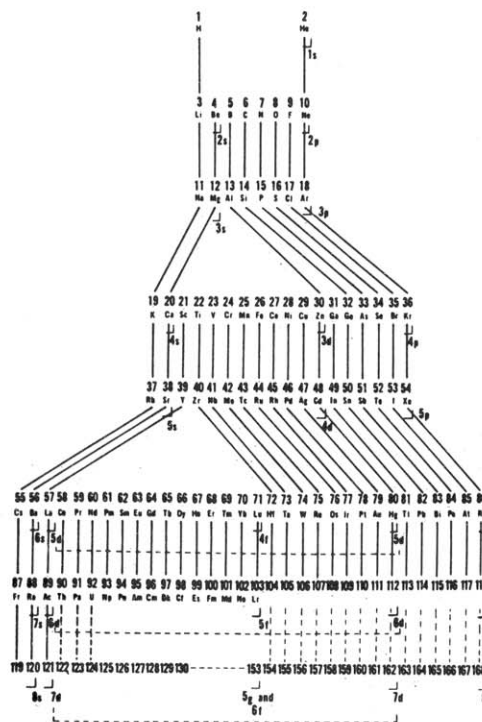

Figure 1. Extended form of the periodic table showing accommodation of the lanthanides and actinides. Reproduced from reference (4).

same type. The *f*-transition series owe their existence to decreases in both the potential energies and spatial extensions of the *f* orbitals immediately after the elements lanthanum and actinium, which allow preferential occupancy of these orbitals by the differentiating electrons. The effect is particularly evident after lanthanum (6–8), where, for example, the binding energy of a single $4f$ electron drops from -0.95 eV for the La atom to -5 eV for the Nd atom. Although the $4f$ orbitals lie well outside the xenon structure in the La atom and are thus unoccupied, they are within that structure in the Nd atom and occupied. The situation is comparable among the succeeding elements. With the actinides, the circumstance is similar but much less pronounced. The net result is difficulty in establishing exact parallels between the lighter lanthanides and the potentially corresponding actinides in both electronic configuration and properties. This difficulty is reduced as the number of $5f$ electrons present increases.

The ground-state electronic configurations and spectroscopic terms characteristic of neutral atoms and cationic species are summarized for the lanthanides (Ln) in Table 3 and for the actinides (An) in Table 4. No absolute regularity in occupancy of orbitals is noted either among the elemental lanthanides or actinides or among cations of small charge. Complete regularity is achieved, however, among the more highly charged species (e.g., Ln^{3+}, An^{3+}, An^{4+}), where all electrons beyond the nf level have been removed. There is a discernible tendency, wherever possible, to achieve the nf^7 and nf^{14} configurations sooner than a strict nuclear charge sequence would dictate. This tendency can be associated with the enhanced spectroscopic stabilities of the half and completely filled sub shells. In Figure 2 (10), a comparison of the energies of the $4f^{n-1}5d^16s^2$ and $5f^{n-1}6d^17s^2$ configurations with those of the $4f^n6s^2$ and $5f^n6s^2$ configurations, respectively, shows this tendency rather clearly.

Comparisons between the lanthanide and actinide series yield the regularities summarized in Table 5. In considering these regularities, one must realize that the data used apply only to the gaseous ions in their lowest energy states and thus do not necessarily reflect observed situations. The $+1$, most of the $+2$, the lighter $+3$ (for the actinides), and the heavier $+4$ (for the actinides) ions have no existence in either solution or crystal lattices. Within these limitations, however, periodicity between ions of the same charge type in a given vertical column of Table 5 may be expected. Periodicity is indeed recognized in several areas of comparative chemistry, some of which are now considered in greater detail.

Oxidation States

Observed oxidation states noted either in solution or in isolable compounds are summarized in Table 6 (1, 11–13). The data summarized in Figure 1 suggest that since less energy is required for the conversion $5f \to 6d$

Table 3. Ground-State Electronic Configurations and Spectroscopic Terms of Lanthanide Species

Atomic number	Symbol	Configuration (Term)			
		Ln^0	Ln^+	Ln^{2+}	Ln^{3+}
57	La	$5d^16s^2(^2D_{3/2})$	$5d^2\ (^3F_2)$	$5d^1(^2D_{3/2})$	$4f^0(^1S_0)$
58	Ce	$4f^15d^16s^2(^1G_4)$	$4f^15d^16s^1(^2G_{7/2})$	$4f^2(^3H_4)$	$4f^1(^2F_{5/2})$
59	Pr	$4f^36s^2(^4I_{9/2})$	$4f^36s^1(^5I_4)$	$4f^3(^4I_{9/2})$	$4f^2(^3H_4)$
60	Nd	$4f^46s^2(^5I_4)$	$4f^46s^1(^6I_{7/2})$	$4f^4(^5I_4)$	$4f^3(^4I_{9/2})$
61	Pm	$4f^56s^2(^6H_{5/2})$	$4f^56s^1(^7H_2)$	$4f^5(^6H_{5/2})$	$4f^4(^5I_4)$
62	Sm	$4f^66s^2(^7F_0)$	$4f^66s^1(^8F_{1/2})$	$4f^6(^7F_0)$	$4f^5(^6H_{5/2})$
63	Eu	$4f^76s^2(^8S_{7/2})$	$4f^76s^1(^9S_4)$	$4f^7(^8S_{7/2})$	$4f^6(^7F_0)$
64	Gd	$4f^75d^16s^2(^9D_2)$	$4f^75d^16s^1(^{10}D_{5/2})$	$4f^75d^1(^9D_2)$	$4f^7(^8S_{7/2})$
65[a]	Tb	$4f^96s^2(^6H_{15/2})$	$4f^96s^1(^7H_8)$	$4f^9(^6H_{15/2})$	$4f^8(^7F_6)$
66	Dy	$4f^{10}6s^2(^5I_8)$	$4f^{10}6s^1(^6I_{17/2})$	$4f^{10}(^5I_8)$	$4f^9(^6H_{15/2})$
67	Ho	$4f^{11}6s^2(^4I_{15/2})$	$4f^{11}6s^1(^5I_8)$	$4f^{11}(^4I_{15/2})$	$4f^{10}(^5I_8)$
68	Er	$4f^{12}6s^2(^3H_6)$	$4f^{12}6s^1(^4H_{13/2})$	$4f^{12}(^3H_6)$	$4f^{11}(^4I_{15/2})$
69	Tm	$4f^{13}6s^2(^2F_{7/2})$	$4f^{13}6s^1(^3F_4)$	$4f^{13}(^2F_{7/2})$	$4f^{12}(^3H_6)$
70	Yb	$4f^{14}6s^2(^1S_0)$	$4f^{14}6s^1(^2S_{1/2})$	$4f^{14}(^1S_0)$	$4f^{13}(^2F_{7/2})$
71	Lu	$4f^{14}5d^16s^2(^2D_{3/2})$	$4f^{14}6s^2(^1S_0)$	$4f^{14}6s^1(^2S_{1/2})$	$4f^{14}(^1S_0)$

[a] Ground states of Tb^0 and Tb^+ may be $4f^85d^16s^2$ and $4f^85d^16s^1$, respectively.

Table 4. Ground-State Electronic Configurations and Spectroscopic Terms of Actinide Species

Atomic number	Symbol	Configuration (Term)[a]				
		An^0	An^+	An^{2+}	An^{3+}	An^{4+}
89	Ac	$6d^17s^2(^2D_{3/2})$	$7s^2(^1S_0)$	$7s^1(^2S_{1/2})$	$5f^0(^1S_0)$	
90	Th	$6d^27s^2(^3F_2)$	$6d^17s^2(^2D_{3/2})$	$6d^2\ (^3F_2)$	$5f^1(^2F_{5/2})$	$5f^0(^1S_0)$
91	Pa	$5f^26d^17s^2(^4K_{11/2})$	$5f^2\ 7s^2(^3H_4)$	$5f^26d^1\ (^4K_{11/2})$	$5f^2(^3H_4)$	$5f^1(^2F_{5/2})$
92	U	$5f^36d^17s^2(^5L_6)$	$5f^3\ 7s^2(^4I_{9/2})$	$5f^4\ (^5I_4)$	$5f^3(^4I_{9/2})$	$5f^2(^3H_4)$
93	Np	$5f^46d^17s^2(^6L_{11/2})$	$5f^4\ 7s^2(^5I_4)$	$5f^5\ (^6H_{5/2})$	$5f^4(^5I_4)$	$5f^3(^4I_{9/2})$
94	Pu	$5f^6\ 7s^2(^7F_0)$	$5f^6\ 7s^1(^8F_{1/2})$	$5f^6\ (^7F_0)$	$5f^5(^6H_{5/2})$	$5f^4(^5I_4)$
95	Am	$5f^7\ 7s^2(^8S_{7/2})$	$5f^7\ 7s^1(^9S_4)$	$5f^7\ (^8S_{7/2})$	$5f^6(^7F_0)$	$5f^5(^6H_{5/2})$
96	Cm	$5f^76d^17s^2(^9D_2)$	$5f^76d^17s^1(^{10}D_{5/2})$	$5f^76d^1\ (^9D_2)$	$5f^7(^8S_{7/2})$	$5f^6(^7F_0)$
97	Bk	$5f^86d^17s^2(^8G_{15/2})$	$5f^86d^17s^1(^9G_8)$	$5f^86d^1\ (^8G_{15/2})$	$5f^8(^7F_6)$	$5f^7(^8S_{7/2})$
98	Cf	$5f^{10}\ 7s^2(^5I_8)$	$5f^{10}\ 7s^1(^6I_{17/2})$	$5f^{10}\ (^5I_8)$	$5f^9(^6H_{15/2})$	$5f^8(^7F_6)$
99	Es	$5f^{11}\ 7s^2(^4I_{15/2})$	$5f^{11}\ 7s^1(^5I_8)$	$5f^{11}\ (^4I_{15/2})$	$5f^{10}(^5I_8)$	$5f^9(^6H_{15/2})$
100	Fm	$5f^{12}\ 7s^2(^3H_6)$	$5f^{12}\ 7s^1(^4H_{13/2})$	$5f^{12}\ (^3H_6)$	$5f^{11}(^4I_{15/2})$	$5f^{10}(^5I_8)$
101	Md	$5f^{13}\ 7s^2(^2F_{7/2})$	$5f^{13}\ 7s^1(^3F_4)$	$5f^{13}\ (^2F_{7/2})$	$5f^{12}(^3H_6)$	$5f^{11}(^4I_{15/2})$
102	No	$5f^{14}\ 7s^2(^1S_0)$	$5f^{14}\ 7s^1(^2S_{1/2})$	$5f^{14}\ (^1S_0)$	$5f^{13}(^2F_{7/2})$	$5f^{12}(^3H_6)$
103	Lr	$5f^{14}6d^17s^2(^2D_{3/2})$	$5f^{14}\ 7s^2(^1S_0)$	$5f^{14}\ 7s^1(^2S_{1/2})$	$5f^{14}(^1S_0)$	$5f^{13}(^2F_{7/2})$

[a] Configurations for U^{2+}, Np^{2+}, Cm^+, Cm^{2+}, Bk^0, Bk^+, Bk^{2+}, Cf^0, Cf^+ inferred.

Table 5. Periodicity of Ground-State Configurations Between Lanthanide and Actinide Series

Species of Comparable Ground-State Configurations

Oxidation state	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Ac					Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
+1	La^+	Ce^+	Pr^+	Nd^+	Pm^+	Sm^+	Eu^+	Gd^+	Tb^+	Dy^+	Ho^+	Er^+	Tm^+	Yb^+	Lu^+
						Pu^+	Am^+	Cm^+	Bk^+	Cf^+	Es^+	Fm^+	Md^+	No^+	Lr^+
+2	La^{2+}	Ce^{2+}	Pr^{2+}	Nd^{2+}	Pm^{2+}	Sm^{2+}	Eu^{2+}	Gd^{2+}	Tb^{2+}	Dy^{2+}	Ho^{2+}	Er^{2+}	Tm^{2+}	Yb^{2+}	Lu^{2+}
				U^{2+}	Np^{2+}	Pu^{2+}	Am^{2+}	Cm^{2+}		Cf^{2+}	Es^{2+}	Fm^{2+}	Md^{2+}	No^{2+}	Lr^{2+}
+3	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
	Ac^{3+}	Th^{3+}	Pa^{3+}	U^{3+}	Np^{3+}	Pu^{3+}	Am^{3+}	Cm^{3+}	Bk^{3+}	Cf^{3+}	Es^{3+}	Fm^{3+}	Md^{3+}	No^{3+}	Lr^{3+}
+4[a]		Ce^{4+}	Pr^{4+}						Tb^{4+}						
		Th^{4+}	Pa^{4+}	U^{4+}	Np^{4+}	Pu^{4+}	Am^{4+}	Cm^{4+}	Bk^{4+}	Cf^{4+}	Es^{4+}	Fm^{4+}	Md^{4+}	No^{4+}	Lr^{4+}

[a] Configurations of Ce^{4+}, Pr^{4+}, and Tb^{4+} are those deemed most probable.
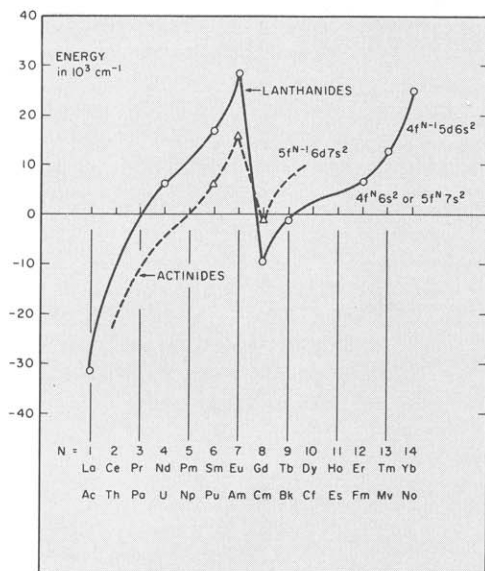

Figure 2. Approximate energy relationships between $f^{n-1}ds^2$ and $f^n s^2$ ground-state configurations. Reproduced from "Lanthanide Actinide Chemistry" (10) with permission of the American Chemical Society.

Table 6. Oxidation States of Lanthanides and Actinides

Symbol (Lanthanides)	+2	+3	+4	Symbol (Actinides)	+2	+3	+4	+5	+6	+7
La		+		Ac		+				
Ce	(+)	+	+	Th	(?)	(?)	+			
Pr		+	(+)	Pa			+	+		
Nd	(+)	+	(+)	U		+	+	+	+	
Pm		+		Np		+	+	+	+	(+)
Sm	(+)	+		Pu		+	+	+	+	(+)
Eu	+	+		Am	(+)	+	+	+	+	
Gd		+		Cm		+	+			
Tb		+	(+)	Bk		+	+			
Dy		+	(+)	Cf	(?)	+				
Ho		+		Es	(?)	+				
Er		+		Fm	(?)	+				
Tm	(+)	+		Md	+	+				
Yb	+	+		No	+	+				
Lu		+		Lr		+				

+, in solution; (+), in solid only; (?), in doubt.

Table 7. Some Comparative Standard Oxidation Potentials

Symbol (Lanthanides)	0–III	II–III	III–IV	Symbol (Actinides)	0–III	II–III	III–IV
La	2.522			Ac	(2.6)		
Ce	2.483		−1.74	Th			
Pr	2.462		(−2.86)	Pa			
Nd	2.431			U	1.80		0.631
Pm	(2.423)			Np	1.83		−0.155
Sm	2.414	1.55		Pu	2.03		−0.982
Eu	2.407	0.43		Am	2.36	>1.5	(−2.80)
Gd	2.397			Cm			(>−2.80)
Tb	2.391			Bk			(−1.6)
Tm	2.278			Md		(0.2)	
Yb	2.267	1.15		No		(−1.4)	

[a] Relative to $E^0 = 0.00$ V for $\frac{1}{2} H_2$ (g) $\rightleftarrows$ H$^+$ (aq) $+ e^-$ at 298°K. Estimated values in parentheses.

than for the conversion $4f \rightarrow 5d$ in the first half of the series, higher oxidation states should, on a comparative basis, be more common for the lower actinides. Correspondingly, the requirement of more energy for the $5f \rightarrow 6d$ conversion than for the $4f \rightarrow 5d$ conversion in the second half of the series should make the lower oxidation states more common for the higher actinides. These expectations are in agreement with the data in Table 6. It is of interest that nobelium(II) has an apparently larger thermodynamic stability in aqueous solution than nobelium(III) (14).

Of course, the observed oxidation states do not, for either series, reflect directly the ground-state configurations of the atoms in question but are determined more by combinations of ionization energies and solvation or lattice energies. The +3 state is, of all possible states, the one common to most of the elements of the two series. In a sense, this almost ubiquitous state is a reflection of periodicity. The absence of complete and accurate oxidation-potential data makes absolute comparisons difficult. Even from the fragmentary data given in Table 7, it is evident that no absolute examples of periodicity between the series can be identified. At best, one can point out that europium(II) and americium(II) show parallelism, as do ytterbium(II) and nobelium(II).

Crystal Radii

For a given oxidation state, there are parallel "contractions" with increasing nuclear charge that reflect the imperfect shielding of f electrons by each other, and the actinide species is always somewhat larger than the formally analogous lanthanide species. These circumstances are shown for the +3 state in Figure 3. The slight, but readily detectable, discontinuity at the Gd^{3+} ion does not have a parallel at the Cm^{3+} ion. Rather there appears to be a continuing divergence in size among the An^{3+} species as nuclear charge continues to increase.

The small differences in crystal radii for a given charge type account for the many observed examples of isostructuralism both within each series and between the two series (1, 3, 11, 15). No more than gross periodicity can be distinguished, however, since there is only general parallelism between the lanthanide and actinide series, and no unique situations can be distinguished.

Magnetic Properties

A comparison of the molar magnetic susceptibilities of the terpositive lanthanide ions and certain actinide
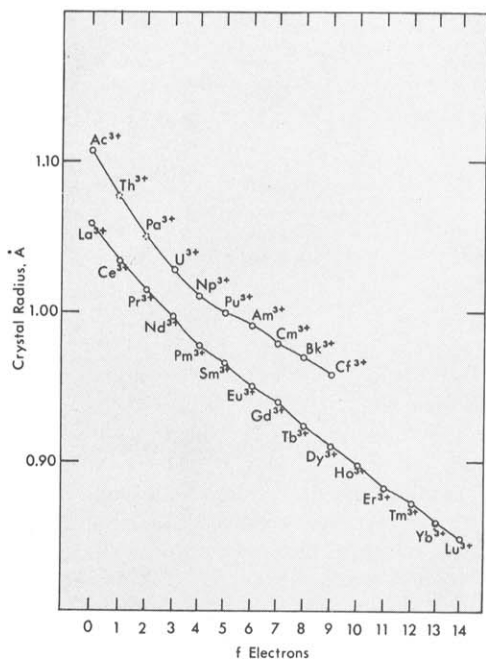
Figure 3. Crystal radii of Ln^{3+} and An^{3+} ions.

Figure 4. Magnetic susceptibilities of Ln^{3+} ions and actinide species containing same numbers of f electrons. Originally from "The Chemistry of the Actinide Elements" (3); adapted on p. 103 "The Chemistry of the Lanthanides" (1). Reproduced by permission of John Wiley & Sons, Inc. and Van Nostrand Reinhold Company.

species with the same number of f electrons is given in Figure 4 (1, 3). There is apparent in this figure a periodicity between iso-f species. However, this periodicity is misleading since the parallelism shown depends completely upon the actinide species selected. Furthermore, it should not be implied that the binodal type curve shown is neither characteristic nor indicative of f-electron species. If one chooses species correctly, he can construct a similar binodal curve for $3d$ ions, even though it is generally stated that susceptibility is always a maximum only for $3d^5$ species (16). The paramagnetic properties are not directly functions of the number of f electrons alone. The complexity of their origins is such that no simple relationships between the two series can be established.

Absorption of Radiant Energy

The absorption spectra of the lanthanide and actinide species are often characterized by line-like bands that result from "forbidden" intra f-f transitions (1, 3). Again the factors that are responsible for energy absorption are so involved that no simple correlation between band positions and ground-state electronic configura-
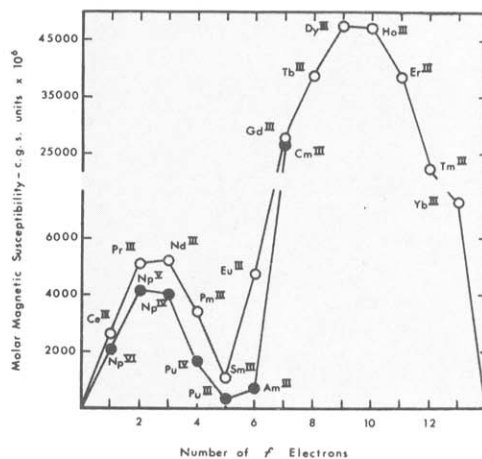
tions of the ions is possible. This situation is illustrated by the comparison between the absorption spectra of the Nd^{3+} and U^{3+} ions, both f^3 species, given in Figure 5.

Chemical Characteristics

Broad periodicity between the two series is indicated by the similarity in reactions of ions of the same charge type with specific reagents. Instances of well-defined periodicity between specific lanthanide and actinide ions are more difficult to establish because differences in properties are more of degree than of kind within either series. However, ion-exchange behavior is selective in the presence of suitable complexing agents and can serve as an illustrative example. The elution data summarized in Figure 6 are cited as a case in point.

Periodicity within the Lanthanide and Actinide Series

Absolute periodicity within either series is extremely difficult to establish since for a given oxidation state there is ordinarily more of a gradation in a specific property from element to element than a regular recurrence. It is reasonable to expect that periodicity is more likely to be observed within the lanthanide series since the distinguishing $4f$ electrons are better shielded
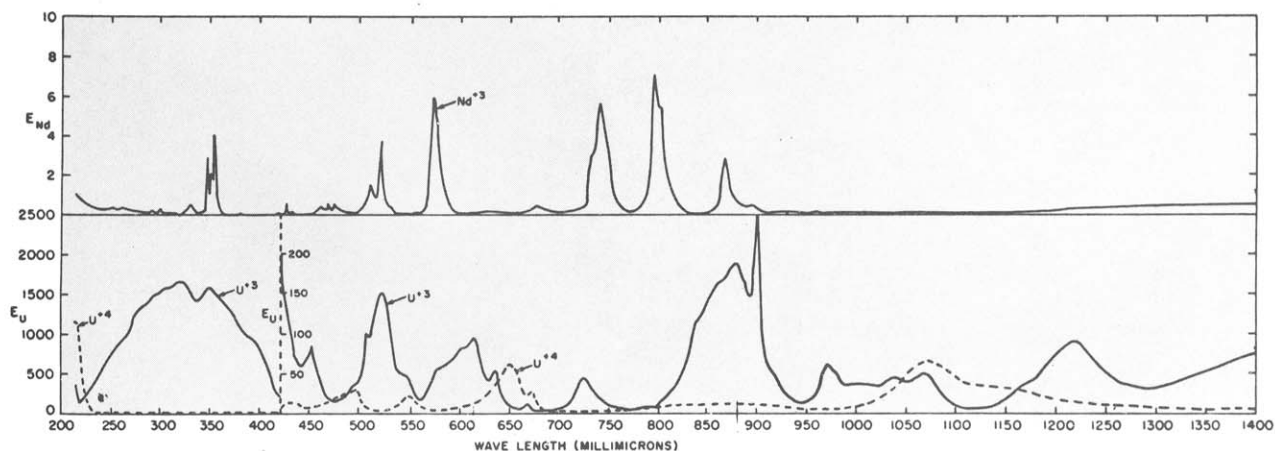

Figure 5. Absorption spectra of the f^3 species Nd^{3+} and U^{3+} and the f^2 species U^{4+} in aqueous hydrochloric acid solution. Reproduced from "The Chemistry of the Actinide Elements" (3) by permission of John Wiley & Sons, Inc.
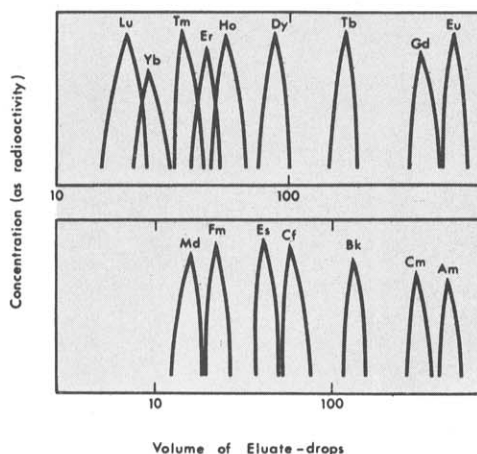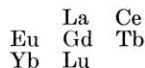
Figure 6. Comparative elution behaviors of Ln^{3+} and An^{3+} ions with α-hydroxyisobutyrate ion. Originally in "The Chemistry of the Actinide Elements" (3); adapted on p. 108 of "The Chemistry of the Lanthanides" (1). Reproduced by permission of John Wiley & Sons, Inc. and Van Nostrand and Reinhold Company.

than the $5f$ electrons and thus better able to behave individually.

Lanthanide Series

Some evidences of periodicity are apparent in the oxidation-state, crystal-radii, and magnetic data previously cited. Preferences for the $4f^0$, $4f^7$, and $4f^{14}$ electronic configurations among the various oxidation states are indicated in Table 8 (1). Thus, it can be said that the periodic arrangement

$$\begin{array}{cc} & \text{La} \quad \text{Ce} \\ \text{Eu} & \text{Gd} \quad \text{Tb} \\ \text{Yb} & \text{Lu} \end{array}$$

is at least reasonable on this basis. The existence of isolable Sm(II), Tm(II), Pr(IV), Nd(IV), and Dy(IV)

compounds and an extension of the regularity developed allow the arrangement

	La	Ce	Pr	Nd	Pm
Sm Eu	Gd	Tb	Dy	Ho	Er
Tm Yb	Lu				
II	III		IV		III

which does bring together elements capable of existing in the same oxidation states. Of course, this, or any other, arrangement does not recognize the fact that the +2 state is achievable for all of the elements by isolation of Ln^{2+} ions in crystals (17).

A classification apparently based upon number of unpaired electrons can be devised in terms of the observation (18) that a terpositive ion with n more electrons than the La^{3+} ion has a color comparable with that of a terpositive ion with $14 - n$ electrons more. This circumstance is indicated in Table 9. Color is, however, a non-quantitative property, and a consideration of the wavelengths of major absorption shows that the arrangement is coincidental. Furthermore, isoelectronic terpositive and non-terpositive ions do not have the same color (e.g., colorless Gd^{3+} and yellowish Eu^{2+}; colorless Lu^{3+} and green Yb^{2+}). The general term designation is comparable for ions containing the same number of unpaired $4f$ electrons.

Chemically, periodicity is not readily distinguishable within the lanthanide series except in the properties associated with differing oxidation states. To some degree, the thermodynamic stabilities, as measured by formation constants (K), or free energy changes, of certain complexes of the Ln^{3+} ions, reflect periodicity between the lighter cations (La^{3+}–Eu^{3+}) and the heavier cations (Gd^{3+}–Lu^{3+}). Curves relating the formation constants of 1:1 complexes with certain aminopolycarboxylates to nuclear charge, and thus indirectly cationic radius, show a discontinuity at the Gd^{3+} ion and in several instances a repetition of stability trends (Figure 7). However, with other ligands, the changes observed may follow other patterns (19, 20). Unfortunately, the thermodynamic stability of an Ln^{3+} ion complex in aqueous solution is determined by a number of factors, among them changes in coordination number that may be functions of the ligand in question and result in the expulsion of differing numbers of water molecules from the coordination sphere of the cation (20). However, elimination of this effect by formation of complex species in dilute aqueous solution by reaction of the ligand with a series of solid salts of the same degree of hydration

$$LnX_3 \cdot 9H_2O(s) + 3L^-(aq) \rightarrow LnL_3^{3-}(aq) +$$
$$3X^-(aq) + 9H_2O(aq)$$

Table 8. Comparison of Electronic Configurations of Various Ions Ln^{n+}

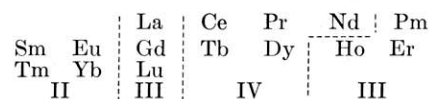| Symbol	Configuration (Examples)			
	0	$+2^a$	$+3$	$+4^a$
La	$5d^16s^2$		$4f^0(La^{3+})$	
Ce	$4f^15d^16s^2$	$4f^2(CeCl_2)$	$4f^1(Ce^{3+})$	$4f^0(CeO_2, CeF_4, Ce^{4+})$
Pr	$4f^3$	$6s^2$	$4f^2(Pr^{3+})$	$4f^1(PrO_2, PrF_4, K_2PrF_6)$
Nd	$4f^4$	$6s^2$ $4f^4(NdI_2)$	$4f^3(Nd^{3+})$	$4f^2(Cs_3NdF_7)$
Pm	$4f^5$	$6s^2$	$4f^4(Pm^{3+})$	
Sm	$4f^6$	$6s^2$ $4f^6(SmX_2, SmO)$	$4f^5(Sm^{3+})$	
Eu	$4f^7$	$6s^2$ $4f^7(Eu^{2+})$	$4f^6(Eu^{3+})$	
Gd	$4f^75d^16s^2$		$4f^7(Gd^{3+})$	
Tb	$4f^9$	$6s^2$	$4f^8(Tb^{3+})$ $4f^7(TbO_2, TbF_4, Cs_3TbF_7)$	
Dy	$4f^{10}$	$6s^2$	$4f^9(Dy^{3+})$ $4f^8(Cs_3DyF_7)$	
Ho	$4f^{11}$	$6s^2$	$4f^{10}(Ho^{3+})$	
Er	$4f^{12}$	$6s^2$	$4f^{11}(Er^{3+})$	
Tm	$4f^{13}$	$6s^2$ $4f^{13}(TmI_2)$	$4f^{12}(Tm^{3+})$	
Yb	$4f^{14}$	$6s^2$ $4f^{14}(YbX_2, Yb^{2+})$	$4f^{13}(Yb^{3+})$	
Lu	$4f^{14}5d^16s^2$		$4f^{14}(Lu^{3+})$	

^{a} Restricted to isolable species.

Table 9. Color and Absorption Spectra of Ln^{3+} Ions as Functions of Number of Unpaired $4f$ Electrons

Ion	Unpaired electrons	Term	Principal absorption bands (Å)	Color	Principal absorption bands (Å)	Term	Unpaired electrons	Ion
La^{3+}	$0(4f^0)$	$^1S_0$	none	colorless	none	$^1S_0$	$0(4f^{14})$	Lu^{3+}
Ce^{3+}	$1(4f^1)$	$^2F_{5/2}$	2105, 2220, 2380, 2520	colorless	9750	$^2F_{7/2}$	$1(4f^{13})$	Yb^{3+}
Pr^{3+}	$2(4f^2)$	$^3H_4$	4445, 4690, 4822, 5885	green	3600, 6825, 7800	$^3H_6$	$2(4f^{12})$	Tm^{3+}
Nd^{3+}	$3(4f^3)$	$^4I_{9/2}$	3540, 5218, 5745, 7395 7420, 7975, 8030, 8680	reddish	3642, 3792, 4870, 5228, 6525	$^4I_{15/2}$	$3(4f^{11})$	Er^{3+}
Pm^{3+}	$4(4f^4)$	$^5I_4$	5485, 5680, 7025, 7355	pink yellow	2870, 3611, 4508, 5370, 6404	$^5I_8$	$4(4f^{10})$	Ho^{3+}
Sm^{3+}	$5(4f^5)$	$^6H_{5/2}$	3625, 3745, 4020	yellow	3504, 3650, 9100	$^6H_{15/2}$	$5(4f^9)$	Dy^{3+}
Eu^{3+}	$6(4f^6)$	$^7F_0$	3755, 3941	colorless^a	2844, 3503, 3677, 4872	$^7F_6$	$6(4f^8)$	Tb^{3+}
Gd^{3+}	$7(4f^7)$	$^8S_{7/2}$	2729, 2733, 2754, 2756	colorless	2729, 2733, 2754, 2756	$^8S_{7/2}$	$7(4f^7)$	Gd^{3+}

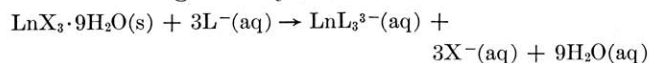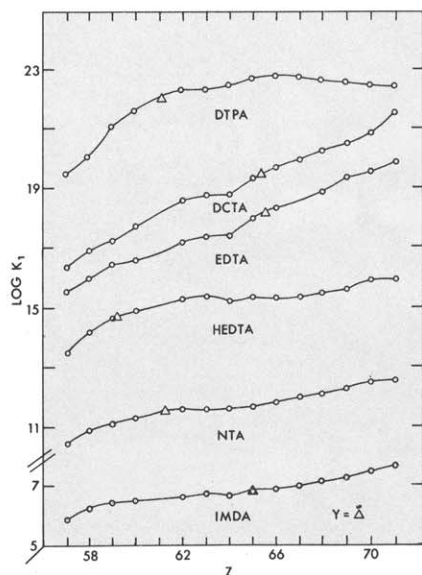^{a} Tb^{3+} may be very pale pink.

Figure 7. Formation constants at 25°C. for 1:1 chelates of Ln^{3+} ions with various aminepolycarboxylate ions (IMDA, iminodiacetate; NTA, nitrilotriacetate; HEDTA, N-hydroxyethylethylenediaminetriacetate; EDTA, ethylenediaminetetraacetate; DCTA, trans-1,2-diaminocyclohexanetetraacetate; DTPA, diethylenetriaminepentaacetate).
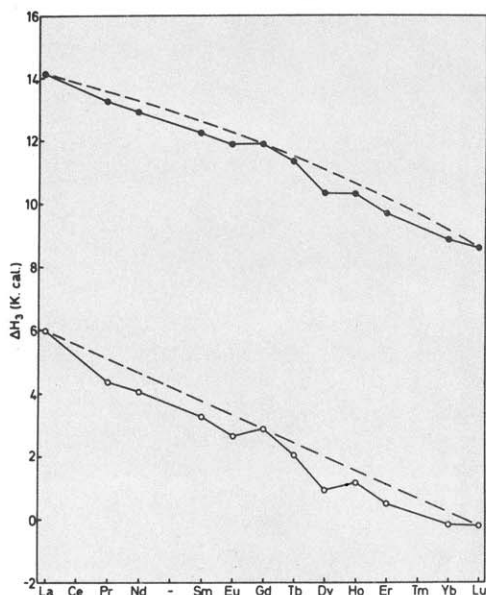

Figure 8. Enthalpy of formation at 25°C. of LnL_3^- chelates (L = diglycollate—top curve; dipicolinate—bottom curve) from the solid salts $Ln(BrO_3)_3 \cdot 9\ H_2O$. Reproduced from reference (21) by permission of Pergamon Press.

where L = diglycollate or dipicolinate and X = bromate or ethylsulfate, gives enthalpies of formation (ΔH_3) that do show periodicity, as indicated for the bromates in Figure 8 (21).

It is of interest also that both the dissociation energies of the gaseous monoxides and the enthalpies of sublimation of the elemental lanthanides vary with atomic number in the same periodic fashion, but to an even greater degree (22). In these cases and in the formation of the diglycollate and dipicolinate complexes, an extra stability appears to characterize the $4f^0$, $4f^7$, and $4f^{14}$ configurations.

As indicated in Table 10, both the metallic radii and the melting points also show periodicity in that maximum

Table 10. Metallic Radii and Melting Points of Lanthanides

Symbol	Radius (Å)	Melting point (°C)	Symbol	Radius (Å)	Melting point (°C)
La	1.877	920	Gd	1.802	1312
Ce	1.824	798	Tb	1.782	1356
Pr	1.828	935	Dy	1.773	1407
Nd	1.822	1016	Ho	1.766	1470
Pm	(1.810)	1168	Er	1.757	1522
Sm	1.802	1072	Tm	1.746	1545
Eu	2.042	826	Yb	1.940	816
			Lu	1.734	1675

values of the former and minimum values of the latter characterize europium and ytterbium, with rather smooth trends elsewhere. Maxima in metallic radii are associated with inherent divalency in the metallic lattices. Minima in melting points may have the same origin. It is perhaps significant that samarium, for which some divalence in the metallic state may be expected, has a lower melting point than promethium. In both sets of properties, lanthanum is apparently somewhat "out of line," probably because of the $4f^0$ ground state that characterizes the lanthanum atom.

Actinide Series

Some of these general considerations apply also to the actinide elements and their ions but in a much less well-defined manner. The greater projection and availability of the 5f orbitals decrease the significance of their contribution to periodicity among these species. It does not seem reasonable, at least in our present state of knowledge, to emphasize periodicity within this series.

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