

Thermodynamics and Biogeochemistry of Lanthanides and Actinides

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The heat capacity (C_{p298}^0) and entropy (S_{298}^0) of elementary substances that occur in a solid, liquid, or gaseous state under standard conditions ($T = 298$ K and $P = 1$ atm) are the only thermodynamic properties of chemical elements that are taken into consideration irrespective of their compounds. In [1, 2], we used their specific values ($\text{J g}^{-1} \text{K}^{-1}$) calculated from [3] and constructed a diagram (Fig. 1) characterizing the periodicity of their variations as a function of even and odd ordinal numbers of elements. The periodicity of specific heat capacity in the diagram is determined by maximum values corresponding to the alkali metals and minimum values corresponding to the noble gases and gaseous halogens (F and Cl). Between these extremes, the heat capacity of elements monotonously diminishes with increasing ordinal numbers. The maximums of entropy fall on the noble gases, while deep entropy minimums divide the chemical elements located in ordinal number ranges between noble gases into light (low heat capacity) and heavy (higher heat capacity) groups. This universal subdivision is fundamental and determines a difference of chemical elements, not only in thermodynamic, but also in metallogenic, biogeochemical, and physical properties. This aspect is considered below for different periods of the chemical element system.

The first and second periods comprise the elements of the lowest heat capacity disposed between helium and neon. The deep entropy minimums in this ordinal number range (2–10) fall on boron (among odd elements) and carbon (among even elements). The left branches of this extreme relationship embrace the elements of hydrogen and helium periods (Li, Be, B, and C) characterized by anomalous thermodynamic properties [2]. For example, in contrast to all other elements, their standard entropy is much lower than the heat capacity. The relatively heavy gases—nitrogen and oxygen—pertain to the right branch.

In the third period (Ne–Ar), the extremum boundaries fall on aluminum and silicon. They separate the relatively light elements of the left branch (Mg, Na, F, and Ne) from the heavier elements of the right branch (P, S, Cl, and Ar), which are substantially distinct in terms of the specific heat capacity.

The fourth period (Ar–Kr) is complicated by the incorporation of the transitional d -elements (^{21}Sc – ^{30}Zn). The development of d -orbitals in the electron structure of the elements is characterized by compaction and decrease of entropy of metals. This is clearly seen in Fig. 1, where the d -elements of this range make up a broad zone of lowered entropy values with a minimum falling on chromium due to the transition of an electron in its structure from s -orbital to d -orbital ($3d^5 4s^1$). This anomaly distinguishes chromium from the adjacent, even transitional, metals, especially from iron ($3d^6 4s^2$). Theoretically, the entropy minimum should fall on iron, as on other metals of its group (Ru and Os), in the succeeding periods.

Ruthenium (in the series of even elements) and rhodium (in the series of odd elements), which occupy the lowest entropy positions in the low-entropy zone of the transitional metals of the fifth period (Kr–Xe), divide the elements of this period into light (oxyphile) and heavy (sulfurophile and siderophile) elements that strongly tend to occur in a native state. The depicted difference between metals of the left and right branches of the studied extreme systems directly follows from thermodynamic analysis of the exchange reactions markedly shifted to the right: $\text{Y}_2\text{S}_3 + \text{In}_2\text{O}_3 \rightarrow \text{Y}_2\text{O}_3 + \text{In}_2\text{S}_3$, $\text{SrS} + \text{CdO} \rightarrow \text{CdS} + \text{SrO}$, and so on. The siderophile affinity of the metals from the right branches is characterized by exchange reactions between intermetallics ($\text{ZrFe} + \text{Pd} \rightarrow \text{PdFe} + \text{Zr}$, and others), while their affinity to noble metals is demonstrated by frequent occurrence in the native state (Pd and Ag). The subdivision of elements in this aspect has a metallogenic implication, because they govern different relationships of light and heavy metals with igneous rocks and different prospecting guides for the respective deposits.

In the sixth period (Xe–Rn), the lowest entropy of Os and Ir is of coordination significance. The left branch of oxyphile metals (relative to these extremes) naturally includes lanthanides (57–70) that pertain to

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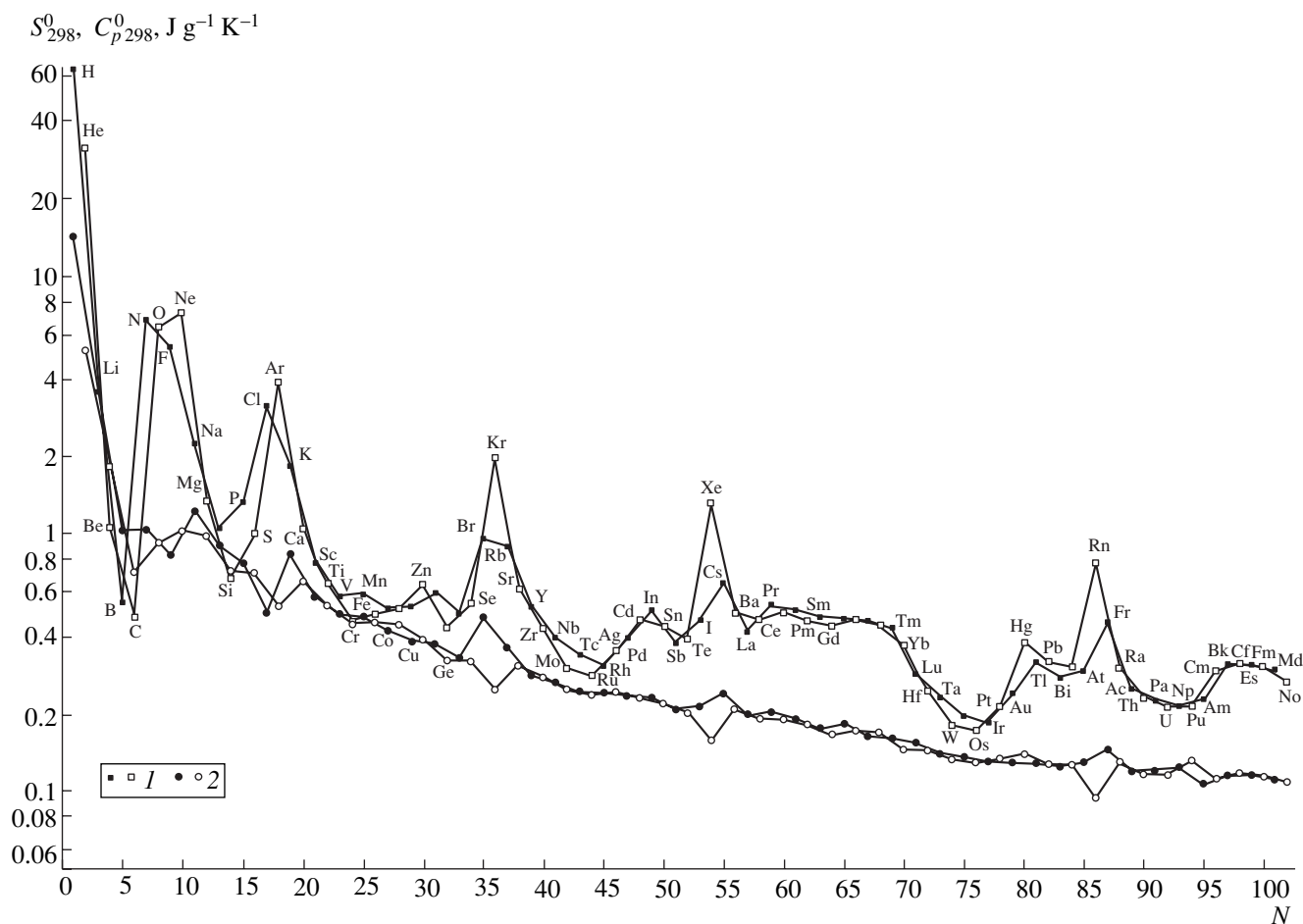


Fig. 1. Periodicity in variation of (1) entropy and (2) heat capacity of elementary substances corresponding to chemical elements with odd (filled symbols) and even (open symbols) ordinal numbers (N). The logarithmic scale of entropy (S_{298}^0) and heat capacity ($C_{p,298}^0$) is used.

f -block elements, although lanthanum is a d -element ($5d^16s^2$). In Fig. 1, La occupies the minimum entropy position, which is a distinctive feature of this element relative to other lanthanides (58–70) that form a gentle dome of the high entropy values. This implies that the f -orbital is opposite to the d -orbital in the thermodynamic sense, and its development in the electron structure was accompanied by an increase in entropy. Therefore, the thermodynamic properties of lanthanides are close to those of high-entropy alkali earth metals. They are united into the family of rare earth elements, in contrast to the low-entropy transitional d -metals.

Actinides occupy analogous positions in the seventh period (Rn–118). However, in contrast to lanthanides, they are clearly subdivided into two families. The first family includes the relatively light low-entropy elements (89–95) and the thermodynamically similar d -element actinium ($6d^17s^2$). The second family includes the high-entropy f -elements (96–102) that correlate with the alkali earth Ra and lanthanides in terms of entropy (Fig. 1).

The low-entropy actinide family comprises both d -elements, such as actinium ($6d^17s^2$) and thorium ($6d^27s^2$), and f -elements characterized by a suppressed impact of f -orbital on entropy. The actinide family retained the low-entropy specifics of d -elements, as has already been pointed out in the literature with respect to protactinium ($5f_26d^17s^2$): as was stated in [4], “the chemical behavior of protactinium is dual: it behaves either as a d -element, similar to tantalum (and was forecast by D.I. Mendeleev to be ecatantalum), or as an f -actinide. This is caused by a minor energy difference between electrons of the $6d$ - and $5f$ -levels.”

Now, we pass to a systematic comparison of lanthanides and actinides. Table 1 demonstrates the specific heat capacity and entropy of metals ($J g^{-1} K^{-1}$), as well as the melting temperature (K) of lanthanides (57–71), actinides (89–102), and the elements (72–88) dividing them. Figure 2 shows the periodicity of entropy variation as a function of ordinal number separately for the metals with odd and even numbers, which differ, according to the Oddo–Harkins rule, in their nat-

Table 1. Specific heat capacity and entropy of metals ($\text{J g}^{-1} \text{K}^{-1}$) and the melting temperature (K) of lanthanides, actinides, and elements between them

Element	C_{p298}^0	S_{298}^0	T	
Lanthanides	⁵⁷ La	0.199	0.413	1193
	⁵⁸ Ce	0.192	0.457	1071
	⁵⁹ Pr	0.202	0.522	1204
	⁶⁰ Ne	0.190	0.492	1289
	⁶¹ Pm	0.190	0.502	1573
	⁶² Sm	0.181	0.453	1345
	⁶³ Eu	0.176	0.468	1090
	⁶⁴ Gd	0.166	0.434	1585
	⁶⁵ Tb	0.182	0.461	1630
	⁶⁶ Dy	0.172	9.464	1682
	⁶⁷ Ho	0.164	0.454	1743
	⁶⁸ Er	0.168	0.263	1797
	⁶⁹ Tm	0.160	0.423	1818
	⁷⁰ Yb	0.145	0.363	1097
⁷¹ Lu	0.154	0.282	1936	
	⁷² Hf	0.144	0.244	2500
	⁷³ Ta	0.140	0.229	3287
	⁷⁴ W	0.132	0.178	3680
	⁷⁵ Re	0.135	0.196	3452
	⁷⁶ Os	0.123	0.171	3300
	⁷⁷ Ir	0.131	0.185	2716
	⁷⁸ Pt	0.133	0.213	2042
	⁷⁹ Au	0.129	0.241	1336
	⁸⁰ Hg	0.139	0.384	234
	⁸¹ Tl	0.129	0.314	577
	⁸² Pb	0.128	0.313	601
	⁸³ Bi	0.124	0.272	545
	⁸⁴ Po	0.126	0.300	527
	⁸⁵ At	0.129	0.289	500
	⁸⁶ Rn	0.0936	0.755	202
	⁸⁷ Fr	0.146	0.447	289
	⁸⁸ Ra	0.130	0.299	1233
	Actinides	⁸⁹ Ac	0.121	0.276
⁹⁰ Th		0.118	0.230	2023
⁹¹ Pa		0.120	0.225	1703
⁹² U		0.116	0.211	1405
⁹³ Np		0.124	0.213	913
⁹⁴ Pu		0.131	0.211	913
⁹⁵ Am		0.106	0.225	1268
⁹⁶ Cm		0.112	0.291	1613
⁹⁷ Bk		0.115	0.308	1259
⁹⁸ Cf		0.117	0.308	1173
⁹⁹ Es		0.115	0.305	–
¹⁰⁰ Fm		0.114	0.301	–
¹⁰¹ Md		0.110	0.292	–
¹⁰² No		0.108	0.263	–

ural abundances. The dashed lines indicate a parity of lanthanides and high-entropy actinides (96–102) that are similar in electron configuration. The low-entropy actinides (89–95), including actinium (89) correlating with lanthanum (57), fit a lower entropy level that corresponds to the transitional *d*-elements rather than the lanthanides. These correlations govern assemblages of low-entropy actinides in the ore deposits. For example, a typical assemblage of gold and uranium is known in many deposits, including the ores of the Witwatersrand deposit (South Africa), which contain more than half of the world gold reserves. According to [5], “intergrowths of bright gold grains with velvet black uraninite are a mineralogical symbol of Witwatersrand.”

The subdivision of actinides in terms of inherent entropy has important biogeochemical implications, because only low-entropy actinides (90–95) take part in microbiological transformation in the geochemical cycle of elements. In contrast to the high-entropy actinides of virtually constant valence equal to three (a four-valent state is recorded only for Cm and Bk), the low-entropy actinides are characterized by various degrees of oxidation: Th(III, IV), Pa (IV, V), U (III, IV, V, VI), Np (III, IV, V, VI, VII), Pu (III, IV, V, VI, VII), and Am (III, IV, V, VI, VII). This is responsible for their similarity to the most biologically active *d*-metals. They are subjected to microbial solubilization and immobilization, including bioaccumulation, biosorption, bioreduction, and biocrystallization [6, 7]. For instance, accumulation of neptunium (the lowest-entropy odd actinide) by *Pseudomonas aeruginosa*, *Streptomyces viridocromogenes*, *Scenedesmus obliquus*, and *Micrococcus luteus* cells may be as much as 10 mg/1 g of the dry cell weight [6]. A chemical and biogeochemical similarity exists between Fe (III), Pu (IV), and Th (IV). Therefore, many Fe-complexing agents are used by microorganisms for formation of complexes with the aforementioned actinides.

Of particular interest is the dissimilatory reduction of actinides by thermophile Fe-reducing microorganisms and their consequent biomineralization [8–10]. The elements subjected to the microbial enzymatic redox transformation, i.e., the transitional metals of the fourth (Cr, Mn, Fe, and Co), fifth (Mo, Te, Pd, and Ag), and sixth (Au) periods, are thus supplemented by the low-entropy actinides of the seventh period (U, Np, and Pu).

Like high-entropy actinides, rare earth elements are involved in biogeochemical processes to a much lesser extent. Therefore, their involvement in the biogeochemical reactions of microbe cells remains poorly studied. However, their similarity to alkali earth metals in the processes of cellular absorption and impact on the conformational changes of biomacromolecules is evident. The replacement of Ca ions (regulators of the activity of some enzymes) by lanthanides is a typical example. If Ca ions are absent, Pr, Nd, Sm, Tb, Dy, Er, and Yb restore the activity of α -amylase in *Bacillus subtilis*

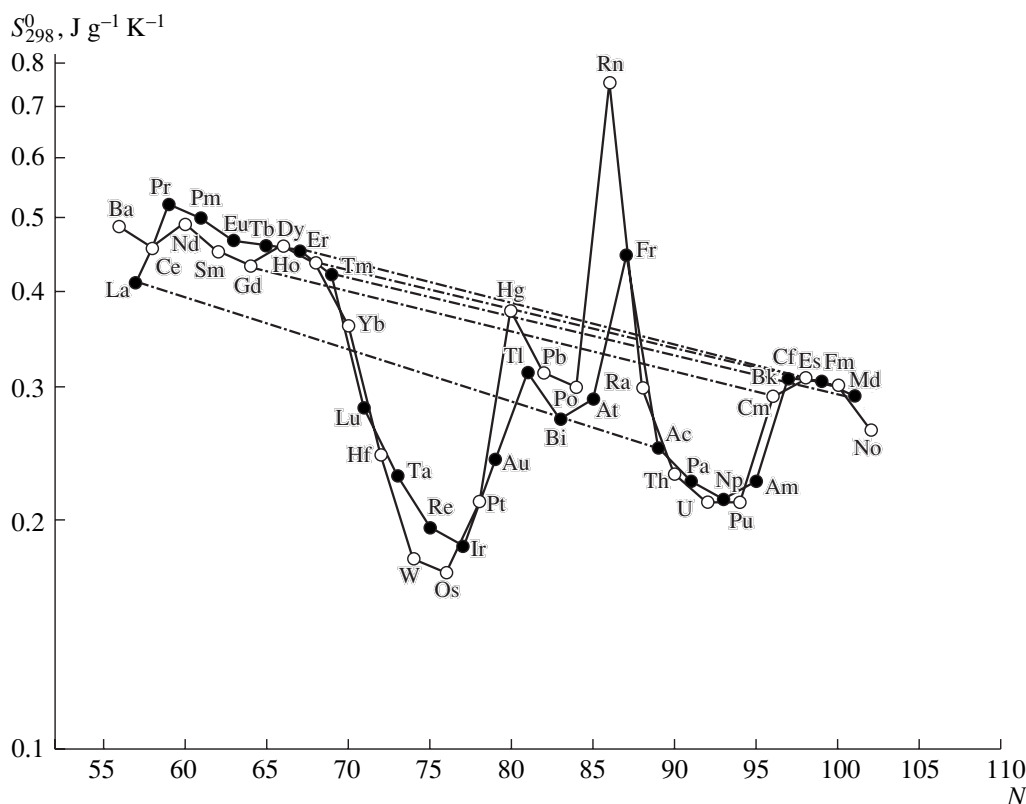


Fig. 2. Correlation of specific entropy of actinides and lanthanides in terms of electron structure shown separately for odd (filled symbols) and even (open symbols) metals (see Table 1).

cells by 33, 43, 56, 76, 77, 78, and 99%, respectively [11]. This is natural, because Yb^{2+} with a completely occupied f -orbital ($\text{Xe}4f^{14}$) is an analog of Ca^{2+} (Ar) in its electron configuration. In the case of enzyme activation and membrane stabilization [12, 13], lanthanides are functionally bound by their thermodynamic correlation (with respect to entropy value) with alkali earth elements (Figs. 1, 2). Europium is among the cofactors that can strongly affect the conformation of macromolecules. This element can activate an alcohol dehydrogenase and radically affect the tertiary and quaternary structure of these enzymes [14].

The melting temperatures of elementary substances corresponding to lanthanides, actinides, and the elements between them reflect a reverse correlation between the melting temperature and entropy of elements. However, this correlation is not rigorous (Figs. 2, 3) and is expressed only in general terms. Europium and ytterbium have an anomalously low melting temperature (Fig. 3). The minimum melting temperatures of europium ($4f^76s^2$) and ytterbium ($4f^{14}6s^2$) are determined by the completeness of f -semi-orbitals ($4f^7$) and orbitals ($4f^{14}$) in their electron configurations. However, these elements do not stand out in terms of maximum entropy. Actinides Am ($5f^77s^2$) and No ($5f^{14}7s^2$), which correspond to these elements in electron structure, differ from the adjacent elements

neither in their minimum melting temperature nor in the maximum entropy of the respective metals.

The aforementioned subdivision of metals by entropy minimums into oxyphile (left branches of dia-

Table 2. Negative values of free energy of the formation of three-valent metal oxides and sulfides (ΔG_{298}^0 , kJ g $^{-1}$)

Metal	Oxide (M_2O_3)	Sulfide (M_2S_3)	Metal	Oxide (M_2O_3)	Sulfide (M_2S_3)
^5B	17.155		^{60}Nd	5.115	2.888
^{13}Al	15.518		^{62}Sm	5.151	
^{21}Sc	13.192		^{63}Eu	4.419	
^{22}Ti	9.972		^{64}Gd	4.779	
^{23}V	7.6		^{65}Tb	4.856	
^{24}Cr	6.928		^{66}Dy	4.749	
^{25}Mn	5.591		^{67}Ho	4.741	
^{26}Fe	4.65	0.731	^{68}Er	4.729	
^{31}Ga	5.326		^{69}Tm	4.651	
^{39}Y	8.045		^{70}Yb	4.382	
^{45}Rh	1.092		^{71}Lu	4.495	
^{49}In	3.0	1.036	^{77}Ir		0.466
^{57}La	5.236	3.135	^{79}Au	+0.178	
^{58}Ce	5.203	3.046	^{81}Tl	0.705	
^{59}Pr	5.218	2.984	^{83}Bi	1.059	0.298
			^{94}Pu	3.003	

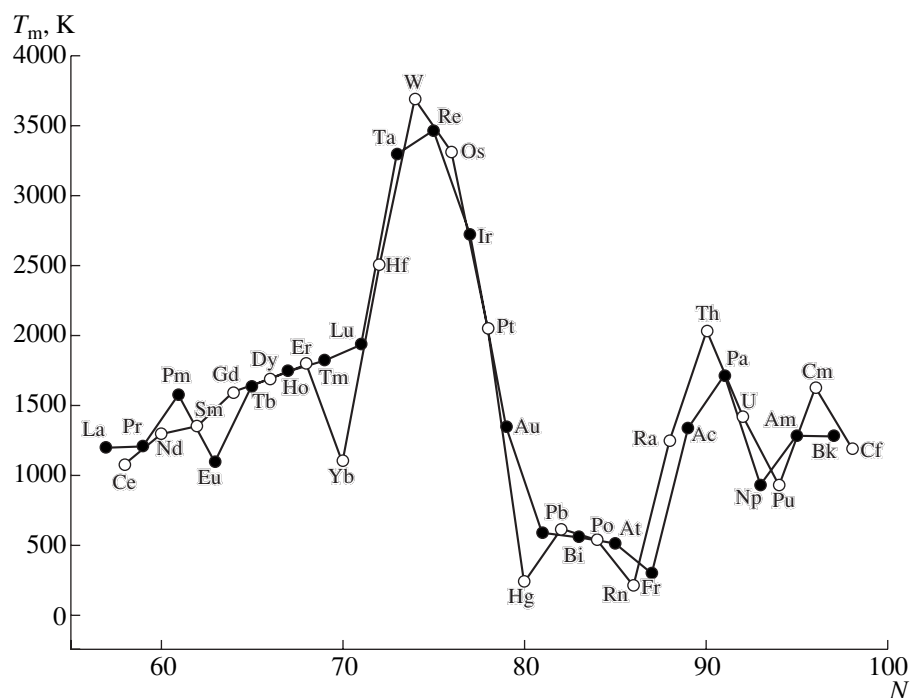


Fig. 3. Comparison of lanthanides, actinides, and elements between them in terms of the melting temperature of corresponding elementary substances. See Fig. 2 for symbols.

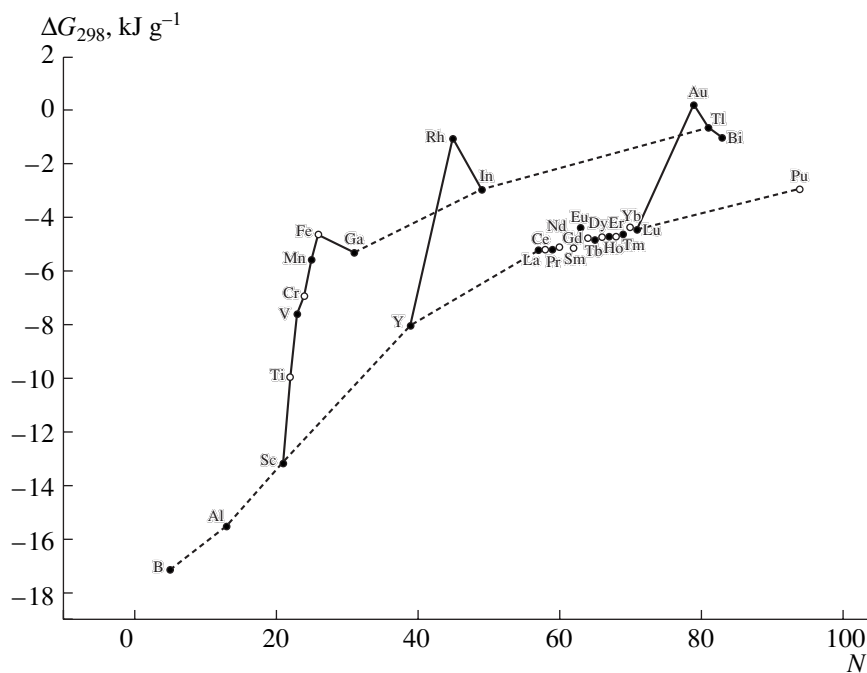


Fig. 4. Correlation of free energy of the formation of three-valent metal oxides (ΔG_{298}) with ordinal numbers (N) of the respective elements. See Fig. 2 for symbols.

grams in Figs. 1 and 2) and sulfurophile (right branches) families is thermodynamically characterized by values of the free energy of oxide and sulfide formation. Table 2 shows these values calculated for 1 g of substance for the three-valent state [3, 15], which is

most typical of lanthanides and actinides. The data on oxides correlate with the ordinal numbers of elements in Fig. 4. They display that actinides and lanthanides belong to the left branches of oxyphile metals of the third group in the periodic system (B–Al–Sc–Y–lan-

thanides–actinides), which are principally different from the sulfurophile and siderophile metals of the right branches (Ga–In–Tl) pertaining to the same third group but having much lower affinity to oxygen. Thus, the free energy of oxide formation (Table 2; Fig. 4) has important implications for metallogenic and biogeochemical subdivision of metals.

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