

**STANDARD REFERENCE EXERGIES OF CHEMICAL ELEMENTS IN THE OCEANIC REFERENCE MEDIUM.
II. ESTIMATION OF THE EQUILIBRIUM OF ECOSPECIES IN THE OCEANIC MEDIUM**

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A refined system (set), as compared to the Ocean-1 and Ocean-2 systems, of equilibrium standard reference exergies of chemical elements, called the Ocean-3 system, has been developed. The exergies forming the Ocean-3 system were calculated with account for the large oceanic ionic-ligand equilibrium between all chemical elements present in the oceanic medium involving about 300 reactions of complexation of elements. The independence of the equilibrium standard reference exergy of an element of its representative ecospecies was substantiated theoretically and supported by a concrete calculation.

In [1], representing a continuation of [2, 3], a refined system (called the Ocean-2 system) of standard reference exergies of chemical elements in the oceanic reference medium was developed on the basis of a simplified chemical approximation. The Ocean-3 system proposed in the present work is a refined version of the Ocean-2 system, developed on the assumption that there exists a chemical equilibrium between a multitude of known ecospecies of elements present in the oceanic medium. The salinity and other parameters of the new reference state oceanic medium (RSOM) are identical to those in the Ocean-2 version [1]. The concentration of elements dissolved in this medium is equal to the concentration of elements dissolved in the standard mean oceanic water (SMOW) [4] having a salinity $S = 35\%$ and pH 7.905.

Since the RSOM represents a concentrated solution (with a concentration of ~ 0.6 M) of electrolytes in water [4, 5], which is known to be homogeneous but not ideal, the activity of species is of importance in this solution. In the equilibrium chemical approximation, the activity coefficients of these species represented in the form of virial series can be chemically interpreted on the assumption that there are dynamic equilibria between additional short-lived ("virtual") species, such as ionic pairs, triple ions, associates, and other clusters, forming the chemical variety [6, 7] of oceanic solutions of electrolytes.

The equilibrium between the ecospecies of all chemical elements present in the RSOM will be called the large oceanic ionic-ligand equilibrium (LOILE). In calculating the LOILE, we divided the chemical elements $\{R\}$ dissolved in the RSOM into dominant and minor elements and assumed that they are separated by a conditional boundary representing their total (gross) concentration, equal to $\sim 10^{-5}$ M. In accordance with this criterion, the following 13 elements will belong, in addition to H and O, among the dominant elements: B, Br, C, Ca, Cl, F, K, Li, Mg, Na, S, Si, Sr. The other elements of the RSOM will be assumed to be minor elements. This division allowed us to initially consider the common (total) equilibrium between the species of the dominant elements and then the partial (separate) equilibria between the ecospecies of the minor elements and all the species of the dominant elements in the RSOM.

Total Equilibrium between the Species of Dominant Elements in the RSOM. It will be assumed that the total equilibrium is the equilibrium between the species of all the dominant elements present in the RSOM. This means that their equilibrium equations [8] or equations of equilibrium mass action law (EMAL) form a unique system of algebraic equations satisfying the conditions of numerical solvability (the conditions of closure and mutual independence), which include numerical constants of the gross concentration $\{a\}$ of the elements $\{R\}$ dissolved in the RSOM and equilibrium constants $\{K\}$ of the reactions of formation of resultant species $\{R_e\}$ from any initial representative eco-

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TABLE 1. Dominant Elements and Their Initial Representative Ecospecies and Gross Concentrations in the RSOM

R	R _{e1}	a, kmole/m ³	R	R _{e1}	a, kmole/m ³
B	B(OH) ₃ ^o	4.26011·10 ⁻⁴	Si	Si(OH) ₄ ^o	1.02024·10 ⁻⁴
Li	Li ⁺	2.652·10 ⁻⁵	Cl	Cl ⁻	0.558551
C	H ₂ CO ₃ ^o	2.3·10 ⁻³	K	K ⁺	0.0104437
F	F ⁻	7.0026·10 ⁻⁵	Ca	Ca ²⁺	0.0105197
Na	Na ⁺	0.479865	Br	Br ⁻	8.581·10 ⁻⁴
Mg	Mg ²⁺	0.0538951	Sr	Sr ²⁺	9.11016·10 ⁻⁵
S	SO ₄ ²⁻	0.0286647			

species playing the role of a complexing agent and a ligand. The initial gross concentrations of the dominant elements present in the RSOM and their initial ecospecies are given in Table 1.

Table 2 presents 28 stoichiometric equations of formation of the ecospecies of 11 dominant elements, except boron and silicon, because the Gibbs energies of formation of borosilicate and siliceous complexes with the participation of elements other than oxygen and hydrogen are not given in the reference books of thermodynamic quantities forming the database of the present work [9, 10]. Therefore, the equilibria of the borosilicate and siliceous species were assumed to be separate and the equilibrium between them and the other elements of the RSOM was disregarded. Table 2 also presents the thermodynamic equilibrium constants of the indicated 28 reactions, calculated using the combination of the characteristics $\Delta_f G_{298}(R_e)$ (taken from [9, 10]) of the species participating in these reactions as reagents and products.

The features of solving the systems of equilibrium equations of complex chemical processes on the basis of the EMAL were considered by us in [8]. The system of 28 equations defining the total equilibrium between the dominant species present in the RSOM (they are given in Table 2) involves 28 unknown characteristics of the completeness of reactions and has a total order of 56. This fairly complex system was solved using the Mathlab-6 program complex.

The results of calculations of the total equilibrium in the RSOM — the partial equilibrium yields of ecospecies with respect to cations (cationic distribution) ε_c and anions (anionic distribution) ε_a — are presented in Table 2, and the equilibrium yields of elements with respect to representative ecospecies are given in Table 3. The data obtained were used as the basis for calculating the corrections to the standard exergies of elements with account for the equilibria between the ecospecies of both the dominant and minor elements.

Calculation of Corrections to the Second-Approximation Standard Reference Exergies of Chemical Elements (Ocean-2 Version) with Account for the Complex Equilibria between Their Ecospecies. In accordance with the preceding, we will consider two stages of deformation of the element R into its final ecospecies: 1) the element R is entirely transformed into any initial representative ecospecies R_{e1} with a concentration equal to its gross concentration in the RSOM; 2) the ecospecies R_{e1} interacts, as a reagent, with other dominant ligands of the RSOM and is transformed into the finite ecospecies of the element R: R_{e2}, R_{e3}, and so on. We determined the residual equilibrium contraction c of the initial ecospecies R_{e1} with account for the material-balance condition:

$$c = a - x_1 - x_2 - \dots \quad (1)$$

The exergy of the element R found under isothermic and, consequently, standard conditions, is calculated on the basis of the representation of the maximum work expended for its transformation as the difference between the total Gibbs energies of this element in the initial and finite states at the second stage of its transformation:

$$\Delta W = G_1 - G_2 \quad (2)$$

Equality (2) can be extended to each chemical element, including the element R being considered. In this case, the correction ΔW can be used as the correction $\Delta W_2(R_{e1})$ to the standard reference exergy $W_2^o(R_{e1})$ of the element R, calculated with the use of R_{e1} selected as the representative exergy of the element R in the Ocean-2 system, in calculating the refined value of $W_3(R)$ of the standard reference exergy of the element R in the system Ocean-3:

TABLE 2. Initial Data and Results of Calculation of the Total Oceanic Equilibrium of Species of Dominant Elements in the RSOM

R	Stoichiometry of formation of the ecospecies R_e	K	$\epsilon_c, \%$	$\epsilon_a, \%$
Na	$\text{Na}^+ + \text{Cl}^- \leftrightarrow \text{NaCl}^\circ$	0.928426	27.80	23.88
Na	$\text{Na}^+ + \text{SO}_4^{2-} \leftrightarrow \text{NaSO}_4^-$	10.064	1.03	17.22
Mg	$\text{Mg}^{2+} + \text{Cl}^- \leftrightarrow \text{MgCl}^+$	0.123214	3.21	0.31
Mg	$\text{Mg}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{MgSO}_4^\circ$	379.8	33.74	63.43
Mg	$\text{Mg}^{2+} + \text{HCO}_3^- \leftrightarrow \text{MgHCO}_3^+$	10.27	0.88	20.65
Mg	$\text{Mg}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{MgCO}_3^\circ$	841.3	0.27	6.38
K	$\text{K}^+ + \text{Cl}^- \leftrightarrow \text{KCl}^\circ$	0.78015	24.35	0.455
K	$\text{K}^+ + \text{SO}_4^{2-} \leftrightarrow \text{KSO}_4^-$	13.76	1.47	0.53
Ca	$\text{Ca}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{CaSO}_4^\circ$	425.83	37.17	13.64
Ca	$\text{Ca}^{2+} + \text{HCO}_3^- \leftrightarrow \text{CaHCO}_3^+$	17.272	1.46	6.66
Ca	$\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3^\circ$	1278	0.41	1.86
Ca	$\text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{Ca}(\text{HCO}_3)_2^\circ$	1646.2	0.19	1.76
C	$\text{H}_2\text{CO}_3^\circ - \text{H}^+ \leftrightarrow \text{HCO}_3^-$	28.959	—	60.32
C	$\text{H}_2\text{CO}_3^\circ - 2\text{H}^+ \leftrightarrow \text{CO}_3^{2-}$	0.10929	—	0.23
Sr	$\text{Sr}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{SrSO}_4^\circ$	749.436	51.12	0.16
Sr	$\text{Sr}^{2+} + \text{HCO}_3^- \leftrightarrow \text{SrHCO}_3^+$	16.28	1.07	0.042
Sr	$\text{Sr}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{SrCO}_3^\circ$	1288.7	0.32	0.013
F	$\text{Na}^+ + \text{F}^- \leftrightarrow \text{NaF}^\circ$	0.19551	$5 \cdot 10^{-4}$	3.13
F	$\text{K}^+ + \text{F}^- \leftrightarrow \text{KF}^\circ$	0.0622566	$15 \cdot 10^{-4}$	0.02
F	$\text{Li}^+ + \text{F}^- \leftrightarrow \text{LiF}^\circ$	0.3952285	0.001	$4 \cdot 10^{-4}$
F	$\text{Mg}^{2+} + \text{F}^- \leftrightarrow \text{MgF}^+$	30.802	0.0625	48.14
F	$\text{Ca}^{2+} + \text{F}^- \leftrightarrow \text{CaF}^+$	6.0633	0.012	1.82
F	$\text{Sr}^{2+} + \text{F}^- \leftrightarrow \text{SrF}^+$	1.941056	0.003	0.004
Li	$\text{Li}^+ + \text{Cl}^- \leftrightarrow \text{LiCl}^\circ$	0.80152	25.18	0.0012
Li	$\text{Li}^+ + \text{SO}_4^{2-} \leftrightarrow \text{LiSO}_4^-$	1.699049	0.18	$1.6 \cdot 10^{-6}$
Li	$2\text{Li}^+ + \text{CO}_3^{2-} \leftrightarrow \text{Li}_2\text{CO}_3^\circ$	0.8886	$6.9 \cdot 10^{-9}$	$8 \cdot 10^{-13}$
Br	$\text{K}^+ + \text{Br}^- \leftrightarrow \text{KBr}^\circ$	0.44	0.023	0.28
Br	$\text{Na}^+ + \text{Br}^- \leftrightarrow \text{NaBr}^\circ$	0.64	0.032	17.88

$$W_3^\circ(\text{R}) = W_2^\circ(\text{R}_{e1}) + \Delta W_2(\text{R}_{e1}) . \quad (3)$$

The calculation of $\Delta W_2(\text{R}_{e1})$ was considered in [3]; therefore, we will restrict our consideration to the finite formula

$$\Delta W_2(\text{R}_{e1}) = -RT \ln \epsilon , \quad (4)$$

where

$$\epsilon = c/a . \quad (5)$$

TABLE 3. Calculated Resulting Characteristics of the LOILE of Representative Ecospecies in the RSOM

R	Re1	ϵ , %	R	Re1	ϵ
Ac	AcSO ₄ ⁺	58.73	Na	Na ⁺	71.14
Ag	AgCl ₂ ⁻	53.85	Nb	NbO ₃ ⁻	86.18
Al	Al(OH) ₃ ⁰	50.7	Nd	NdSO ₄ ⁺	58.83
As	HAsO ₄ ²⁻	85.49	Ni	NiCl ₂ ⁰	29.39
Au	AuCl ₂ ⁻	99.976	Os	H ₃ OsO ₆ ⁻	69.97
B	B(OH) ₃ ⁰	93.46	P	HPO ₄ ²⁻	83.35
Ba	Ba ²⁺	45.06	Pa	Pa ³⁺	100
Be	Be(OH) ₂ ⁰	83.13	Pb	HPbO ₂ ⁻	99.98
Bi	BiO ⁺	100	Pd	Pd(OH) ₂ ⁰	64.59
Br	Br ⁻	81.84	Pr	PrSO ₄ ⁺	56.11
Ca	Ca ²⁺	60.77	Pt	Pt(OH) ₂ ⁰	100
Cd	CdCl ₂ ⁰	59.2	Ra	Ra ²⁺	100
Ce	CeSO ₄ ⁺	55.27	Rb	Rb ⁺	88.74
Cl	Cl ⁻	75.35	Re	ReO ₄ ⁻	100
Co	Co ²⁺	61.23	Rh	Rh(OH) ₃ ⁰	100
Cr	CrO ₄ ²⁻	96.19	Ru	RuO ₄ ⁻	99.81
Cs	Cs ⁺	84.41	S	MgSO ₄ ⁺	63.43
Cu	Cu(OH) ₂ ⁰	85.93	Sb	H ₃ SbO ₄ ⁰	100
Dy	DySO ₄ ⁺	53.58	Sc	ScHPO ₄ ⁺	79.8
Er	ErSO ₄ ⁺	56.41	Se	SeO ₄ ²⁻	100
Eu	EuSO ₄ ⁺	77.76	Si	Si(OH) ₄ ⁰	98.74
F	F ⁻	46.89	Sm	SmSO ₄ ⁺	59.25
Fe	Fe(OH) ₃ ⁰	100	Sn	Sn(OH) ₄ ⁰	100
Ga	Ga(OH) ₄ ⁻	91.88	Sr	Sr ²⁺	47.48
Gd	GdSO ₄ ⁺	55.63	Ta	HTaO ₃ ⁰	79.86
Ge	Ge(OH) ₄ ⁰	87.60	Tb	TbSO ₄ ⁺	55.42
Hf	Hf(OH) ₄ ⁰	100	Te	HTeO ₃ ⁻	36.8
Hg	HgCl ₄ ²⁻	57.37	Th	Th(OH) ₂ ²⁺	99.99
Ho	HoSO ₄ ⁺	59.34	Ti	Ti(OH) ₄ ⁰	100
I	IO ₃ ⁻	100	Tl	Tl(OH) ₃ ⁰	96.94
In	In(OH) ₃ ⁰	100	Tm	TmSO ₄ ⁺	77.26
Ir	Ir(OH) ₄ ⁰	100	U	UO ₂ (CO ₃) ₂ ²⁻	74.23
K	K ⁺	74.16	V	H ₂ VO ₄ ⁻	47.09
La	LaCO ₃ ⁰	95.03	W	WO ₄ ²⁻	100
Li	Li ⁺	74.64	Y	YSO ₄ ⁺	42.07
Lu	LuSO ₄ ⁺	65.605	Yb	YbSO ₄ ⁺	59.40
Mg	Mg ²⁺	61.84	Zn	ZnCl ⁺	28.65
Mn	Mn(OH) ₄ ⁰	100	Zr	Zr(OH) ₄ ⁰	100
Mo	MoO ₄ ²⁻	99.97			

A distinctive feature of the equilibrium standard reference exergy $W_3^0(R)$ of the element R in the Ocean-3 system is its independence of the choice of its initial representative species Re_1 at the first stage of transformation of this element since the Gibbs function is the state function of a physicochemical system. The numerical value of the change in the Gibbs function is determined by only the initial and final states of a physicochemical system in the case of its reversible transformation under isobaric-isothermal conditions and is independent of the method of this transformation

TABLE 4. Refined Data on the Standard Reference Exergies of Chemical Elements in the Oceanic Medium with a Salinity of 35‰ and a pH of 7.905 Determined with Account for the Equilibria between the Species (Ocean-3 Version)

R	$W_2^{\circ}(R_{e1}),$ kJ/(mole-atom)	$\Delta W_2(R_{e1}),$ kJ/(mole-atom)	$W_3^{\circ}(R),$ kJ/(mole-atom)	$w_3^{\circ}(R),$ MJ/kg	$\phi_d(R),$ V
1	2	3	4	5	6
Ac	970.6	1.3	971.9	4.28	-3.358
Ag	81.8	1.5	83.3	0.773	-0.864
Al	806.9	1.7	808.6	29.97	-2.793
As	489.3	0.4	489.7	6.535	-1.015
Au	31.1	0	31.1	0.158	-0.322
B	629.1	0.2	629.2	58.20	-2.174
Ba	731.7	2.0	733.7	5.343	-3.802
Be	599.2	0.5	599.7	66.54	-3.108
Bi	289.2	0	289.2	1.384	-0.999
Br	49.1	0.5	49.6	0.621	0.514
C	410.4	0	410.4	34.17	-1.063
Ca	709.3	1.2	710.5	17.73	-3.682
Cd	285.9	1.3	287.2	2.555	-1.488
Ce	963.2	1.5	964.6	6.885	-3.333
Cl	60.1	0.7	60.8	1.715	0.630
Co	259.8	1.2	261	4.428	-1.352
Cr	621.4	0.1	621.5	11.95	-1.073
Cs	413.4	0.4	413.8	3.114	-4.289
Cu	138.5	0.5	138.9	2.186	-0.720
Dy	948.2	1.5	949.7	5.845	-3.281
Er	958.1	1.4	959.5	5.737	-3.315
Eu	869.8	0.6	870.4	5.728	-3.007
F	231.1	1.9	233	12.263	2.415
Fe	371.4	0	371.4	6.651	-1.283
Ga	523.3	0.2	523.5	7.509	-1.809
Gd	947.2	1.4	948.6	6.033	-3.277
Ge	546.4	0.3	546.8	7.530	-1.417
H	117.6	0	117.6	116.7	-1.219
Hf	1088.1	0	1088.1	6.096	-2.819
Hg	129.8	1.4	131.1	0.654	-0.679
Ho	975.9	1.3	977.2	5.925	-3.376
I	81.5	0	81.5	0.642	-0.169
In	452.9	0	452.9	3.944	-1.565
Ir	228.9	0	228.9	1.191	-0.593
K	366.0	0.7	366.7	9.379	-3.801
La	977.2	0.1	977.3	7.035	-3.376
Li	391	0.7	391.7	56.44	-4.060
Lu	923	1.0	924	5.281	-3.192
Mg	609.8	1.2	611	25.14	-3.166
Mn	464.4	0	464.4	8.453	-2.203
Mo	722.8	0	722.8	7.534	-1.249
Na	336.5	0.8	337.4	14.676	-3.497
Nb	934.6	0.4	935	10.063	-1.938
Nd	954.6	1.3	955.9	6.627	-3.302
Ni	237	3.0	240	4.090	-1.244

Continuation of Table 4

1	2	3	4	5	6
Os	369.2	0.9	370.1	1.946	-0.479
P	848.9	0.45	849.35	27.42	-1.761
Pa	733.7	0	733.7	3.176	-2.535
Pb	268.2	0	268.2	1.294	-1.39
Pd	117.7	1.1	118.8	1.116	-0.615
Pr	966.5	1.4	968	6.870	-3.344
Pt	101.6	0	101.6	0.521	-0.526
Ra	788.8	0	788.8	3.49	-4.087
Rb	389.5	0.3	389.8	4.561	-4.04
Re	687.4	0	687.4	3.691	-1.018
Rh	159.8	0	159.8	1.552	-0.552
Ru	237.5	0	237.6	2.35	-0.352
S	596.7	1.1	597.9	18.65	-1.032
Sb	460.6	0	460.6	3.783	-0.955
Sc	885.3	0.6	885.8	19.7	-3.060
Se	335.2	0	335.2	4.244	-0.579
Si	854.3	0.03	854.3	30.42	-2.213
Sm	950.9	1.3	952.2	6.333	-3.290
Sn	538.8	0	538.8	4.539	-1.396
Sr	732.2	1.85	734.1	8.378	-3.804
Ta	1075.6	0.5	1076.1	5.947	-2.231
Tb	956.2	1.5	957.6	6.026	-3.308
Te	324.7	2.5	327.15	2.564	-0.669
Th	1144.5	0	1144.5	4.932	-2.965
Ti	896.2	0	896.2	18.718	-2.322
Tl	164.7	0.1	164.8	0.806	-1.708
Tm	961.7	0.6	962.4	5.697	-3.325
U	1170.8	0.7	1171.6	4.922	-2.023
V	746	1.9	747.8	14.68	-1.55
W	834	0	834	4.536	-1.44
Y	967.1	2.1	969.3	10.902	-3.349
Yb	931.4	1.3	932.7	5.390	-3.222
Zn	339.6	3.1	342.7	5.241	-1.1776
Zr	1044.3	0	1044.3	11.45	-2.706

(i.e., the method by which the work is done or the method of dividing the process into stages). The choice of R_{e1} , R_{e2} , or R_{e3} at the first stage of transformation of the element R, as its alternative representative ecospecies, determines only the new ways of attainment of a chemical equilibrium in the RSOM, whereas the equilibrium composition of the RSOM or the finite state of the system are independent of the order of appearance of species: R_{e1} , R_{e2} , R_{e3} , and so on, in the process of attainment of this equilibrium. Therefore, the standard reference exergy $W_3^\circ(R)$ of the element R in the Ocean-3 system is independent of the choice of its representative ecospecies, which is expressed in the following form:

$$W_3^\circ(R) = W_2^\circ(R_{e1}) + \Delta W_2(R_{e1}) = W_2^\circ(R_{e2}) + \Delta W_2(R_{e2}) = \dots \quad (6)$$

The quantity $W_3^\circ(R)$ was calculated by formula (3) with the use of the values of $W_2^\circ(R_{e1})$ taken from [1], and the quantity $W_2^\circ(R_{e1})$ was determined from (4) with the use of the ε values taken from Table 3. The results of these calculations are given in Table 4. This table also presents the refined values of the specific exergies $w_3^\circ(R)$ and the deformation potential $\phi_d(R)$ of chemical elements in the Ocean-3 system, determined by the formulas

$$w_3^\circ(\mathbf{R}) = W_3^\circ(\mathbf{R})/M(\mathbf{R}), \quad \varphi_d(\mathbf{R}) = -W_3^\circ(\mathbf{R})/[zF]. \quad (7)$$

It should be noted that the equilibrium standard reference exergies of all species present in the RSOM are invariant only in the case where their thermodynamic characteristics are mutually coordinated. When the indicated quantities are calculated with accidental errors, the exergy of an element $W_3^\circ(\mathbf{R}_{ej})$ is calculated by each ecospecies \mathbf{R}_{ej} characterized by the yield ε_j , and then its mean-weighted value is determined as

$$W_3^\circ(\mathbf{R}) = \sum_j W_3^\circ(\mathbf{R}_{ej}) \varepsilon_j. \quad (8)$$

Note also that, in the case where there are equilibria with the participation of species with different degrees of oxidation, i.e., with a varying value of z , the calculation of the mean-weighted value of $\varphi_d(\mathbf{R})$ is analogous to the calculation of $W_3^\circ(\mathbf{R})$:

$$\varphi_d(\mathbf{R}) = - \sum_j W_3^\circ(\mathbf{R}_{ej}) \varepsilon_j / z_j. \quad (9)$$

Partial (Separate) Equilibria between the Ecospecies of Minor Elements in the RSOM. According to [4], the concentrations of all stable nonradioactive and long-lived radioactive natural elements present in the RSOM are known. The data for Ac and Pa are given in [5]. The minor elements comprise more than 80% of the total number of the chemical elements present in this medium; therefore, consideration of the equilibrium complexation of their ecospecies, in which the ecospecies of dominant elements also participate, is a complex problem that has yet to be solved for the LOILE [4]. In fact, a system of equilibrium equations, the stoichiometric matrix of which has an order of 250–300 and a total order of 500–600, should be solved. As we know, special programs or program packages, which could be used directly for solving this problem, are absent. However, the indicated problem becomes simpler if, instead of the total equilibrium between the minor elements, partial or separate equilibria between the species of one minor element, selected in any order, and all the dominant ligands of the RSOM, defined by stoichiometric equations and corresponding equilibrium equations, are considered. Moreover, the order of each equilibrium equation can be decreased to the first order and the system of linear equilibrium equations obtained in this case can be solved by hand using the substitution method. The point is that the concentration of minor elements is frequently lower than the concentration of dominant species-ligands by 5–6 orders of magnitude or more. In this case, the concentration of dominant ligands changes by a relatively small value in the process of complexation of minor elements; therefore, it can be assumed to be constant and, together with the equilibrium constant, can be united into a new conditional equilibrium constant, which makes it possible to eventually obtain a linear equilibrium equation.

We will illustrate the aforesaid with the example of an arbitrarily selected minor element — actinium (Ac). This element begins the list of elements presented in Table 4; its gross concentration is equal to $a \approx 1.8 \cdot 10^{-19}$ M [4] and the work of its dissolution is $W_{\text{dis}}^\circ = -RT^\circ \ln a = 107.05$ kJ/mole. According to [9], the probable ecospecies of Ac are the ion Ac^{3+} and the complexes AcF^{2+} , AcFe_2^+ , AcF_3° , AcCl^{2+} , AcCl_2^+ , AcSO_4^+ , and $\text{Ac}(\text{SO}_4)_2^-$.

Using the data of [9], we will calculate the equilibrium constants of formation of halogenous complexes of $\{\text{Ac}^{3+}\}$ and the ligands $\{\text{F}^-\}$, $\{\text{Cl}^-\}$, and $\{\text{SO}_4^{2-}\}$. The concentrations of the latter, denoted by b_1 , b_2 , and b_3 , are assumed to be equal to the equilibrium concentrations of the free ions $\{\text{F}^-\}$, $\{\text{Cl}^-\}$, and $\{\text{SO}_4^{2-}\}$, determined in the process of calculating, with the use of a computer, the total equilibrium between the species of dominant elements presented in Table 2, according to which $b_1 = 3.2835 \cdot 10^{-5}$ M, $b_2 = 0.4208777$ M, and $b_3 = 1.43646 \cdot 10^{-3}$ M. It is seen that these concentrations exceed the concentration of Ac in the RSOM by 14–18 orders of magnitude and, consequently, the system of equilibrium equations of the ecospecies of Ac in the RSOM can be, as was noted above, linearized. Using the standard free Gibbs energies of formation of species, presented in [9, 10], we obtained the following equilibrium constants of formation of the alternative ecospecies of Ac:

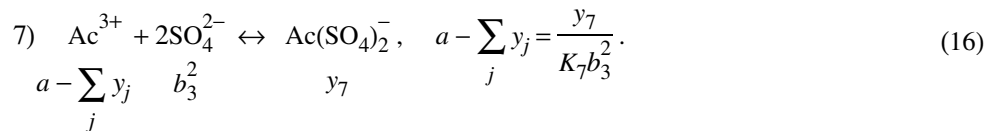
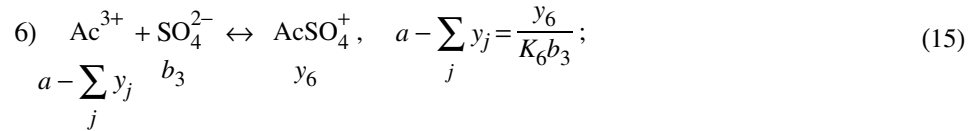
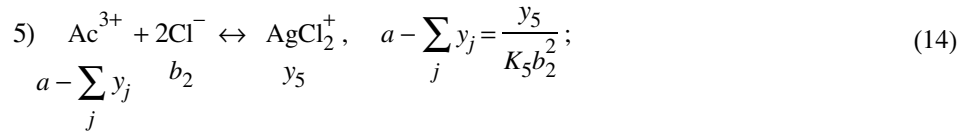
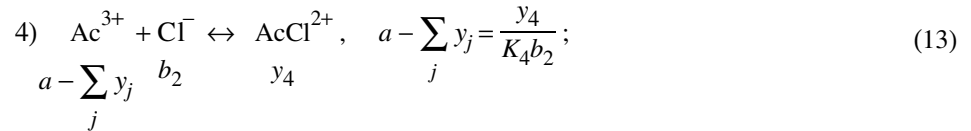
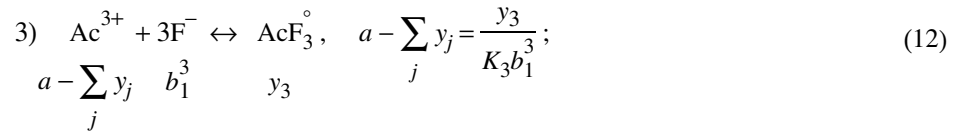
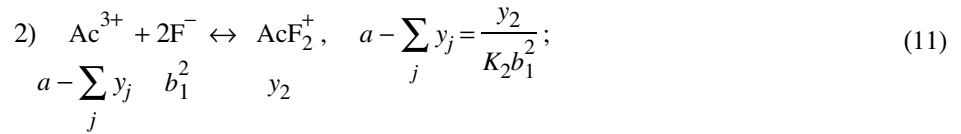
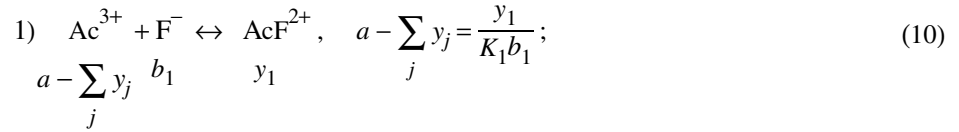
$$K_1 = K(\text{AcF}^{2+}) = 1870.94; \quad K_2 = K(\text{AcF}_2^+) = 1.10424 \cdot 10^6; \quad K_3 = K(\text{AcF}_3^\circ) = 3.9203 \cdot 10^8;$$

$$K_4 = K(\text{AcCl}^{2+}) = 6.525; \quad K_5 = K(\text{AcCl}_2^+) = 8.1116; \quad K_6 = K(\text{AcSO}_4^+) = 6.51215 \cdot 10^3;$$

$$K_7 = K[\text{Ac}(\text{SO}_4)_2^-] = 6.44 \cdot 10^5.$$

The equations of stoichiometry, material balance [8], and equilibrium of the process of formation of complexes of the ion $\{\text{Ac}^{3+}\}$ with the ligands $\{\text{F}^-\}$, $\{\text{Cl}^-\}$, and $\{\text{SO}_4^{2-}\}$, in which the equilibrium concentrations of the species formed are denoted by $\{y_j, j=1, \dots, 7\}$, have the form:

stoichiometry of the process equilibrium equations



From Eqs. (10)–(16) we obtain the following system of equilibrium equations:

$$\begin{aligned}
[1 + (K_1 b_1)^{-1}] y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 &= a, \\
y_1 + [1 + (K_2 b_1^2)^{-1}] y_2 + y_3 + y_4 + y_5 + y_6 + y_7 &= a, \\
y_1 + y_2 + [1 + (K_3 b_1^3)^{-1}] y_3 + y_4 + y_5 + y_6 + y_7 &= a, \\
y_1 + y_2 + y_3 + [1 + (K_4 b_2)^{-1}] y_4 + y_5 + y_6 + y_7 &= a, \\
y_1 + y_2 + y_3 + y_4 + [1 + (K_5 b_2^2)^{-1}] y_5 + y_6 + y_7 &= a, \\
y_1 + y_2 + y_3 + y_4 + y_5 + [1 + (K_6 b_3)^{-1}] y_6 + y_7 &= a, \\
y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + [1 + (K_7 b_3^2)^{-1}] y_7 &= a.
\end{aligned}$$

Below is the solution of this system.

1. The main determinant of the system is equal to

$$\begin{aligned}
A = 1 + K_1 b_1 + K_2 b_1^2 + K_3 b_1^3 + K_4 b_2 + K_5 b_2^2 + K_6 b_3 + K_7 b_3^2 &= 1 + 0.06087 + 0.0011689 + 0.0000135 + \\
+ 2.74623 + 1.436875 + 9.354444 + 1.32896 &= 15.926568.
\end{aligned}$$

Note that, in the linearized equilibrium equations, the yields of ecospecies of elements are independent of their gross concentration a .

2. The equilibrium yields of species (distributions of actinium in species) are equal, in % , to

$$\begin{aligned}
\{Ac^{3+}\} &= 1/A = 6.28, \quad \{AcF^{2+}\} = K_1 b_1 / A = 0.382, \\
\{AcF_2^+\} &= K_2 b_1^2 / A = 0.007, \quad \{AcF_3^\circ\} = K_3 b_1^3 / A = 10^{-4}, \\
\{AcCl^{2+}\} &= K_4 b_2 / A = 17.2418, \quad \{AcCl_2^+\} = K_5 b_2^2 / A = 9.02, \\
\{AcSO_4^+\} &= K_6 b_3 / A = 58.727, \quad \{Ac(SO_4)_2^-\} = K_7 b_3^2 / A = 8.34.
\end{aligned}$$

The standard exergies $W_3^\circ(Ac)$ of elements in the Ocean-3 system are calculated by two methods with the use, alternately, of the two dominant ecospecies $\{AcSO_4^+\}$ and $\{AcCl^{2+}\}$ as the initial representative species.

Variant 1. The species $\{AcSO_4^+\}$ is used as the initial representative species of Ac. The value of $W_2^\circ(AcSO_4^+)$ calculated in [1] for this case is equal to

$$W_2^\circ(AcSO_4^+) = 970.62 \text{ kJ/mole}.$$

The correction $\Delta W_2(AcSO_4^+)$ for this variant is determined from (4) and (5) with the use of the above-indicated value of $\varepsilon = 58.727\%$ obtained from the system of equations (10)–(16):

$$\Delta W_2(AcSO_4^+) = -2.47892 \ln 0.58727 = 1.32 \text{ kJ/mole}.$$

The desired standard reference exergy of actinium in variant 1 of the Ocean-3 version is equal to

$$W_3^\circ(AcSO_4^+) = 970.62 + 1.32 = 971.94 \text{ kJ/mole}.$$

Variant 2. The species $\{AcCl^{2+}\}$ is used as an initial representative species of Ac. Since the species $\{AcCl^{2+}\}$ was not used in [1] as a representative species, the value of $W_2^\circ(AcCl^{2+})$ will be calculated by formula (6) from [1] for the variant considered at $\Delta_f G_{298}^\circ(AcCl^{2+}) = 776.13 \text{ kJ/mole}$ [9]:

$$W_2^\circ(\text{AcCl}^{2+}) = 776.13 + 72.60539 \cdot 3 - 133.40573 + 107.05 = 967.59 \text{ kJ/mole} .$$

Using the above-indicated equilibrium value of the yield of a species $\varepsilon = 17.242\%$ and relation (4), we obtain

$$\Delta W_2(\text{AcCl}^{2+}) = -2.47892 \ln 0.17241 = 4.3577 \approx 4.36 \text{ kJ/mole} .$$

The desired value of the standard reference exergy of actinium, determined in variant 2 of the Ocean-3 version, is equal to

$$W_3^\circ(\text{AcCl}^{2+}) = 967.59 + 4.36 = 971.95 \text{ kJ/mole} .$$

It is seen that the values of the standard reference exergy of actinium, determined in the cases where the different initial representative species $\{\text{AcSO}_4^+\}$ and $\{\text{AcCl}^{2+}\}$ were used, are equal within the round-off error, which is consistent with the above-described invariance properties of equilibrium exergies in the Ocean-3 system and formula (6). This is clear evidence of the fact that the reference exergy of elements is independent of the choice of their representative species R_{ej} if exact values of the Gibbs energies of formation of these elements $\Delta_f G_{298}^\circ(R_{ej})$ and of their equilibrium yields ε_j are known.

Analogous calculations were carried out by us for all elements, the necessary chemical and thermodynamic characteristics of which were known; the results of these calculations are presented in Table 4.

Discussion of Results. The following results of the present investigation, along with the results obtained in [1], are the most important.

First, it has been established that the equilibrium standard reference exergies of elements are independent of the choice of the initial reference species when the characteristics $\Delta_f G_{298}^\circ$ of their species and the total equilibrium composition of the RSOM are correctly estimated.

Second, it is seen from Table 4 that the corrections to the Ocean-2 version made in the process of development of the Ocean-3 version do not exceed 1 kJ/mole-atom in the majority of cases, i.e., they are fairly small. Therefore, the characteristics of the Ocean-2 system described in [1] can be extended in actuality to the Ocean-3 system, which can be considered as a completed system admitting any practical applications, as also the Ocean-2 system; the Ocean-3 system differs from the Ocean-2 system mainly by a higher accuracy. It should be noted that, according to [9, 10], the thermodynamic characteristics of the species of a number of elements, such as Ag, Se, Cu, Hg, La, Ce, Pd, Th, Te, and U, are very different. We used the thermodynamic constants of substances given in [9].

It is interesting to represent the standard mole-atomic exergies, the specific exergies, and the deformation potentials of elements in a ranked form. The elements having maximum mole-atomic exergies (in kJ/mole-atom) are U (1171.6), Th (1144.5), Hf (1088.1), Ta (1076.1), and Zr (1044.3), and the elements having (according to [1]) minimum mole-atomic exergies are N_2 (0.346), O_2 (1.977), Ar (11.668), He (30.386), Au (31.1), Kr (34.134), Ne (34.144), Xe (40.37), Br (49.6), Ag (83.3), and I (81.5). The elements having maximum specific exergies (in MJ/kg) are H_2 (116.7), Be (66.54), B (58.2), Li (56.44), C (34.17), Si (30.42), and Al (29.97), and the elements having minimum specific exergies are N_2 (0.025), O_2 (0.12), Au (0.16), Pt (0.521), Br (0.621), and I (0.642). The elements having minimum deformation potentials (in V) are Cs (-4.289), Ra (-4.087), Li (-4.060), Rb (-4.04), Sr (-3.804), Ba (-3.802), K (-3.801), Ca (-3.682), and Na (-3.497), the elements having maximum deformation potentials are F (+2.415), Cl (+0.630), and Br (+0.514), and the elements having a deformation potential close to zero are I (-0.169), Au (-0.322), Ru (-0.352), Os (-0.479), and Pt (-0.526).

In the process of development of the Ocean-3 oceanic system of exergies of elements, we were short of experimental data on the thermodynamic characteristics of the hydroxide, chloride, and sulphate complexes Sn (4+), Sb (5+), Mn (3+), and Mn (4+); platinides; and carbonated complexes of lanthanoids and actinoids.

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NOTATION

A , determinant of the system of equilibrium equations of ecospecies; a , total (gross) concentration of an element in the oceanic medium, kmole/m³; b , concentration of a liquid, kmole/m³; c , residual equilibrium concentration of the initial ecospecies; F , Faraday number equal to 96.487 kC; G_1 and G_2 , total Gibbs energies at the beginning and end of the second stage of deformation of the element R; $\Delta_f G_{298}^\circ(R_e)$, standard reference Gibbs energy of formation of the ecospecies R_e ; K , K_1 , K_2 , ..., equilibrium constants of formation of an ecospecies; 1st, 2nd, and so forth ecospecies; $M(R)$, molar mass of the element R; R , universal gas constant; R , chemical element whose exergy is calculated; R_e , R_{e1} , R_{e2} , R_{e3} , and R_{ej} , ecospecies of the element R; S , salinity, g/kg or ‰ (pro mille); T , temperature, K; $w_3(R)$, specific exergy of the element R in the Ocean-3 system, MJ/kg; $W_2(R)$, standard molar reference exergy of the element R in the Ocean-2 system, kJ/mole-atom; $\Delta W_2(R)$, correction to an exergy in the Ocean-2 system obtained by calculating its refined value in the Ocean-3 system; kJ/mole-atom; $W_3^\circ(R)$, molar standard reference exergy of the element R in the Ocean-3 system, kJ/mole-atom; $W_3^\circ(R_{ej})$, standard molar reference exergy of the element R calculated by its j th ecospecies R; x_1 , x_2 , and so on, change in the concentration of the representative ecospecies R_{e1} at the second stage of deformation of the element R due to the formation of the 2nd, 3rd, and so forth ecospecies respectively; y_1 , y_2 , and so on, equilibrium concentrations of the ecospecies R_{e2} , R_{e3} , and so on at the second stage of deformation of the element R; z (z_j), degree of oxidation of the element R in an ecospecies (j th ecospecies); ε (ε_j), equilibrium yield of a representative ecospecies (j th ecospecies), rel. units; φ_d , φ_{dj} , deformation potentials of representative ecospecies, V; Δ , change in a thermodynamic characteristic (Gibbs energy) denoted by $\Delta_f G_{298}^\circ$. Subscripts: a, anion; c, cation; d, deformation reaction; dis, dissolution or dissolution from the standard to the environmental concentration; e, ecospecies or ecostate of a species; f, reaction of formation of species from elements; j, index of a ligands or an ecospecies; z, z_j , degrees of oxidation of the element R in ecospecies; 2 and 3, values calculated using the Ocean-2 and Ocean-3 versions. Superscripts: $^\circ$, standard state of a species with respect to its pressure or concentration; $^\circ$ in formulas of species, neutral charge,

REFERENCES

1. G. F. Pinaev, Standard reference exergies of chemical elements in the oceanic reference medium. I. Consideration of modern hydrochemical data on the concentrations of elements in the oceanic medium and the deviation of its reactivity from the neutral one, *Inzh.-Fiz. Zh.*, **79**, No. 5, 180–189 (2006).
2. G. F. Pinaev, Analysis and improvement of the system of standard exergies of chemical elements, in: *Sviridov's Readings* [in Russian], Issue 1, BGU, Minsk (2004), pp. 9–16.
3. G. F. Pinaev, Oceanic system of standard exergies of chemical elements, *Zh. Fiz. Khim.*, **79**, No. 11, 2082–2093 (2005).
4. *Encyclopedia of Ocean Sciences*, Vol. 1–6, Academic Press, Elsevier (2001).
5. N. I. Popov, K. N. Fedorov, and V. M. Orlov, *Sea Water* [in Russian], Nauka, Moscow (1979).
6. R. M. Garrels and C. L. Christ, *Solutions, Minerals, Equilibria* [Russian translation], Mir, Moscow (1968).
7. V. I. Il'ichev (Ed.), *The Chemistry of Sea Water and Authigenous Formation of Minerals* [in Russian], Nauka, Moscow (1989).
8. G. F. Pinaev and V. V. Pechkovskii, *Principles of the Theory of Chemical-Technological Processes* [in Russian], Vyshéishaya Shkola, Minsk (1973), pp. 125–130.
9. V. P. Glushko (Ed.), *Thermal Constants of Substances. Handbook* [in Russian], Issues 1–10, Izd. AN SSSR, VINITI, Moscow (1962–1982).
10. G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovskii, *Handbook of Thermodynamic Quantities* [in Russian], Atomizdat, Moscow (1971).