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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 THEIR REACTIVITY FROM THE NEUTRAL ONE

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A system (set) of standard reference exergies of chemical elements, called the Ocean-2 system, is presented. It includes refined exergies of nine atmospheric elements and 79 elements dissolved in the oceanic water with S = 35‰, pH 7.905, a standard temperature of 298.15 K, and a standard pressure of 101.325 kPa. These exergies were calculated in a simplified chemical approximation with the use of a unique representative species for each element, selected by thermodynamic sifting. The suggestion has been made that the Ocean-2 system of standard reference exergies is close to the lithospheric system.

Introduction. In recent years, the exergetic method has found wide use in thermodynamic analysis of the efficiency of power plants, chemical-engineering plants, and industrial systems as well as in analysis of the action of industrial, agricultural, and life-support enterprises on the environment. Suffice it to say that only on the Internet site of the Elsevier publishing house are there reports on more than 1000 works in which this method was used. However, as was shown in [1–5], the sets of standard exergies of chemical elements [6–8], forming the basis of the exergetic method, are not sufficiently correct. The aim of the present work is to refine these sets for the purpose of increasing the objectivity of the exergic analysis of industrial and environmental processes.

This work is a continuation of our earlier works. In [4], we determined a set of standard exergies of elements in the neutral oceanic water with pH 7.00, called the Ocean-1 system, with the use of the data on their concentrations obtained in [9] in the first approximation. However, as was shown in [5], the actual averaged value of pH is equal to 7.095. Because of this, the aim of the present work was to refine the standard molar-atomic exergies of elements determined in [1–5] on the basis of recent thermodynamic and oceanographic data [9–13].

The following comments on the terminology being used are necessary. In chemical thermodynamics, it is generally agreed that the "standard" thermodynamic characteristic of a substance (species) is a quantity defining this substance at a standard total pressure $\overset{\circ}{P}$ = 101,325 kPa if the substance is a gas or a quantity defining it at a standard thermodynamic activity (concentration) $\overset{\circ}{C}$ = 1 kmole/m^3 (1 mole/liter) if the substance is a liquid solution. In these cases, the temperature of a substance T can be arbitrary (this should be indicated). In the case where the temperature of a substance is also standard (T = 298.15 K), the quantities characterizing this substance are called references in the English-language literature. We considered this case in the present work.

The system of reference exergies of 92 chemical elements obtained in [8] on the basis of the data of [10] is an extension of the system of exergies of 79 elements obtained in [7]. Both systems can be called lithospheric-heterophase systems because, in them, for all elements other than atmospheric elements, solid phases of constant composition — natural minerals or artificial (chemical) solid phases — are used as reference substances. The *lithospheric-heterophase* system replaced the earlier *lithospheric-homophase* system [6] in which natural minerals representing lithospheric ideal solid solutions were used as reference substances. It is evident that both systems of exergies [6, 7] are inadequate to define technogenic and global environmental processes occurring with the participation of the World Ocean, occupying more than 70% of the Earth's surface, including 96% of the water reserves, and representing a terminal "envi-

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ronmental shed" for all technogenic chemical elements of the planet. Because of this, the ocean can be considered as a reference medium, i.e., as an independent reference system of exergies. This generates a need for development of a specific *oceanic* system of standard reference exergies of chemical elements.

The exergies of elements in the sea-water system were calculated for the first time in [14]. However, only the exergies of 24 elements among the known 80 stable or long-lived elements were determined in this work; therefore, the oceanological system of standard exergies developed in [14] cannot be considered as a complete system. Moreover, in [14], an algorithm for calculating the exergies of sea-water elements in this system was not described.

The accuracy of determining the exergies of elements in the oceanic system depends on the certainty of identification of the species of these elements and the exactness of calculating their equilibrium concentrations and activity coefficients as well as standard reference Gibbs energies of formation of the ecospecies of the indicated elements. It should be noted that the concentrations of many elements change with depth; therefore, the standard mean oceanic water (SMOW) is used as a reference medium in oceanology [11]. Samples of the SMOW can be samples of water taken at a depth of about 1900 m in an open part of an ocean. The key physicochemical parameters of the SMOW are its salinity S, temperature t, reactivity pH, and total pressure P. At present, the following values of these parameters are used [9, 11]: $S = 35$ ‰, $t = 3.8^{o}$C (~277 K), and $P \approx 19.7$ MPa [11]. As for the pH value of the SMOW, the problem is not only in the geographic and bathymetric variability of this value but also in the existence of three substantially different scales for measuring the pH value of sea water [12]. The simplest assumption that the pH value of sea water is equal to 7.00 was used by us earlier in the process of development of the Ocean-1 set of reference exergies of elements [4]. In the present work, we used pH 7.905, obtained by averaging of the pH values of different oceans [11].

To correctly determine the exergies of elements in the oceanic system, we used not the SMOW as a reference medium but a peculiar artificial, even if very close to the SMOW, medium that was called the Reference State Oceanic Medium (RSOM). This medium differs from the SMOW by the temperature $\overset{\circ}{T} = 298.15$ K (25^{o}C) and pressure $\overset{\circ}{P} = 101{,}325$ kPa, used as the reference temperature and pressure in the atmospheric system of exergies [6–8], because any system of exergies, including the oceanic one, should be compatible with the atmospheric system. Therefore, the RSOM was used as the reference medium in the Ocean-2 system of exergies developed in the present work. It is assumed that the element composition of the RSOM is identical to that of the SMOW, its temperature is equal to 298.15 K, the pressure in the RSOM is $1.01325{\cdot}10^{5}$ Pa, the activity of ions (except H^{+} and OH^{-}) is negligibly small, $a_{H_2O} = 0.9813$ [11], the pressure of the saturated vapor of H_2O above the oceanic water with a temperature of 25^{o}C and $S = 35$‰ is equal to 3109.36 Pa, the product of the activities of the water ions $K_w = 0.988{\cdot}10^{-14}$ [11], the activity of the H^{+} ion at pH 7.905 is equal to $a_H = \exp_{10}(-7.905) = 1.2445146{\cdot}10^{-8}$ M, the activity of the OH^{-} ion is equal to $a_{OH} = K_w a^{2}_{H_2O}/a_H = 7.6447{\cdot}10^{-7}$ M, and the density of the water is $1.023375{\cdot}10^{3}$ kg/m^{3} [11]; the concentrations of elements in the SMOW and RSOM were taken from [9], and the concentrations of Ac and Pa were taken from [11].

It is assumed, as in [3], that the exergy of an element in the Ocean-2 system is equal to the work of a galvanic cell consisting of an air (O_2) electrode and an element (R) electrode, immersed in the RSOM. The O_2 electrode offers advantages over the H_2 electrode [13] because of the presence of O_2 in the atmosphere and, as a consequence, its priority as a reference substance, which was used in [2–5] for the development of the methodology of calculating standard exergies of elements in the oceanic reference system. It should be noted in this connection that the use of H_2 in [13] as a reference led to the appearance of a systematic error in calculating the exergies of all elements of the oceanic system, and this error was equal to the error in calculating the standard exergies of hydrogen.

In view of the foregoing, we will assume that the standard reference exergy $\overset{\circ}{W}(\mathrm{R})$ of any chemical element R in the Ocean-2 system is equal to the change in the Gibbs energy (taken with the opposite sign) in the process of one-stage transformation of this element (found initially in the standard reference state $\overset{\circ}{\mathrm{R}}$) into the representative environmental species (ecospecies) R_e or into the complex $R_e = \{RO_fL_n\}^{k}_{e}$ formed according to the stoichiometric equation of the half-reaction occurring at a reversible R-element anode immersed in the RSOM:

$$[\overset{\circ}{\mathrm{R}}] + 2f\{\mathrm{OH}^{-}\}_{e} + n\{\mathrm{L}^{-}\}_{e} \Leftrightarrow \{\mathrm{RO}_f\mathrm{L}_n\}^{k}_{e} + f\{\mathrm{H_2O}\}_{e} + z\{\mathrm{e}^{-}\}_{e}\,. \tag{1}$$

The choice of the representative ecospecies R_e influences the desired value of the standard reference exergy of the element R. To correctly select R_e for the element R, it is necessary to have information on the dominant spe-

TABLE 1. Thermodynamic and Environmental Characteristics of Ligands in the Composition of Possible Ecospecies of Elements in the Air (O_2) and in the Oceanic Water

Reactant of deformation half-reactions	$\Delta_f G^\circ_{298}$, kJ/mole	a_e, rel. units, C_e, kmole/m^3	W°_{dis}, kJ/mole	G_e, kJ/mole
O_2^*, g	0	0.202856 (a_e)	3.9545	–3.9545
H_2O, aq	–237.1784	0.9813 (a_e)	0.04679	–237.2252
H^+, aq	0	$1.244515 \cdot 10^{-8}$	45.1212	45.1212
OH^-, aq	–157.2933	$7.6447 \cdot 10^{-7}$	34.9133	–192.2066
F^-, aq	–279.9933	$3.2835 \cdot 10^{-5}$	25.5924	–305.5857
Cl^-, aq	–131.2604	0.420878	2.1453	–133.4057
Br^-, aq	–104.2234	$7.0227 \cdot 10^{-4}$	17.9999	–122.2233
HCO_3^- , aq	–586.8478	$1.3874 \cdot 10^{-3}$	16.3121	–603.1599
CO_3^{2-} , aq	–527.8953	$5.236 \cdot 10^{-6}$	30.1435	–558.0388
SO_4^{2-} , aq	–743.8315	$1.43646 \cdot 10^{-3}$	16.2260	–760.0575
$H_2PO_4^-$, aq	–1130.3913	$3.41072 \cdot 10^{-7}$	36.9141	–1167.3054
HPO_4^{2-} , aq	–1089.263	$1.70741 \cdot 10^{-6}$	32.9214	–1122.1844
PO_4^{3-} , aq	–1018.804	$6.21317 \cdot 10^{-11}$	58.2591	–1077.0631

Note. *)Gas phase; the other species represent an infinitely diluted water solution.

cies of this element in the RSOM (the corresponding data are presented in [9, 11]). The ecospecies R_e can be selected even more exactly on the basis of calculation of the equilibrium between all the species of the element R in the RSOM. Half-reaction (1) is supplemented with the half-reaction at an oxygen cathode (common for all elements) immersed in the RSOM:

$$\frac{1}{4}(O_2)_e + \frac{1}{2}\left\{H_2O\right\}_e + \left\{e^-\right\}_e \Leftrightarrow \left\{OH^-\right\}_e , \tag{2}$$

from which the chemical potential $G_e(e^-)$ or $(-\Phi)$ of the hydrated electrons in the ecostate and the change in the chemical potential of the OH^- ion in the process of oxolation Ψ are calculated from the expressions

$$G_e\,(e^-) = G_e\,(OH^-) - \frac{1}{2}\,G_e\,(H_2O) - \frac{1}{4}\,G_e\,(O_2) = -\,\Phi , \tag{3}$$

$$\Psi = -\,2G_e\,(OH^-) + G_e\,(H_2O)\,. \tag{4}$$

The quantities $G_e(OH^-)$, $G_e(H_2O)$, and $G_e(O_2)$ are determined from the relation

$$G_e\,(A_j) = \Delta_f G^\circ_{298}\,(A_j) + RT \ln a_e\,(A_j) = \Delta_f G^\circ_{298}\,(A_j) + RT \ln C_e\,(A_j)\,. \tag{5}$$

The values of Φ and Ψ depend on the salinity and pH of the RSOM. Using the above-indicated parameters of the RSOM and the $\Delta_f G^\circ_{298}$ values taken from [13], we calculated the environmental thermodynamic characteristics of O_2, H_2O, and OH^- (they are presented in Table 1) and the values of Φ and Ψ: Φ = 72.60539 kJ/mole and Ψ = 147.88038 kJ/mole.

In accordance with (1)–(5), we divided the molar standard exergies $W^\circ(R)$ of the element R into the chemical exergies $W^\circ_{ch}(R)$ and the work of dissolution $W^\circ_{dis}(R)$:

TABLE 2. Standard Reference Exergies of Chemical Elements Present in the Atmosphere

R	R_e	P_e(R), %	$\Delta_f \overset{\circ}{G}_{298}(R_e)$, kJ/mole	$\overset{\circ}{W}_{ch}$(R), kJ/mole-atom	$\overset{\circ}{W}_{dis}$(R), kJ/mole	$\overset{\circ}{W}$(R), kJ/mole-atom	w°(R), MJ/kg
He	He	$4.943 \cdot 10^{-4}$	0	0	30.286	30.29	7.567
C	CO_2	0.032	–394.37	390.42	19.95	410.37	34.166
N	N_2	75.628	0	0	0.6925	0.346	0.0247
O	O_2	20.2856	0	0	3.9545	1.9773	0.124
Ne	Ne	$1.56 \cdot 10^{-4}$	0	0	33.1445	33.14	1.6425
Ar	Ar	0.9033	0	0	11.668	11.67	0.292
Kr	Kr	$1.047 \cdot 10^{-4}$	0	0	34.1343	34.134	0.407
Xe	Xe	$8.454 \cdot 10^{-6}$	0	0	40.37	40.4	0.307
Rn	Rn	$5.815 \cdot 10^{-18}$	0	0	109.79	109.8	0.484

$$\overset{\circ}{W}(\mathrm{R}) = \overset{\circ}{W}_{ch}(\mathrm{R}) + \overset{\circ}{W}_{dis}(\mathrm{R}), \tag{6}$$

where the first term is independent of the ecoconcentration C_e(R) and is determined by the quantity $\Delta_f \overset{\circ}{C}_{298}(R_e)$ or $\Delta_f \overset{\circ}{G}\left[\{RO_f L_n\}_e^k, \text{aq}, 298.15\ \text{K}\right]$ — the standard Gibbs energy of formation of the representative ecospecies of the element R — and can be calculated according to [3] as

$$\overset{\circ}{W}_{ch}(\mathrm{R}) = -\Delta_f \overset{\circ}{G}_{298}(R_e) + \Phi z - \Psi f + G_e(L^-)\, n. \tag{7}$$

The quantity $G_e(L^-)$ was calculated using the data from [10, 13], and the concentrations (activities) of HCO_3^- and CO_3^{2-} were taken from [9] and [11]. The values of $G_e(L^-)$ obtained are presented in Table 1.

The second term in (6) defines the work expended for the dissolution of the ecospecies from the standard concentration (activity) to the environmental one:

$$\overset{\circ}{W}_{dis}(\mathrm{R}) = -RT \ln C_e(\mathrm{R}) = -2.47892 \ln C_e(\mathrm{R}). \tag{8}$$

For the gases present in the atmosphere, the relative pressure P_e(R) is used in (8) instead of C_e(R), and $a_{H_2O} = 0.9813$ for H_2O in the RSOM.

The standard exergies of nine elements comprising the *atmospheric system* are given in Table 2. These elements are present in the atmosphere in the form of gases characterized by $\overset{\circ}{W}_{ch}(\mathrm{R}) = 0$ because they are chemical elements in the reference state. The one exception is C, which is present in the atmosphere in the form of the compound CO_2.

Let us calculate the exergy of C as an atmospheric element (in kJ/mole):

$$\overset{\circ}{W}(\text{C, graphite}) = -\Delta_f \overset{\circ}{G}_{298}(CO_2) - \overset{\circ}{W}(O_2) + \overset{\circ}{W}_{dis}(CO_2) = 394.37434 - 3.9545164 + 19.94958 \approx 410.4.$$

Hydrogen is considered as a hydrospheric element because it is a constituent of oceanic (liquid) water, and its standard exergy is determined from the expression (in kJ/mole of H_2)

$$\overset{\circ}{W}(H_2) = -\Delta_f \overset{\circ}{G}_{298}(H_2O, \text{liq}) - \frac{1}{2}\overset{\circ}{W}(O_2) + \overset{\circ}{W}_{dis}(H_2O, \text{liq}) =$$

$$= 237.1784 - \frac{1}{2}3.9545164 - 2.47892 \ln 0.9813 \approx 235.25.$$

Table 2 also presents the standard reference exergies of atmospheric elements (J/kg), determined as

$$w^{\circ}(\mathrm{R}) = W^{\circ}(\mathrm{R})/M(\mathrm{R})\,. \tag{9}$$

The computational apparatus proposed allows one to calculate, in a corresponding approximation, the standard exergies of all elements whose representative ecospecies $\mathrm{R_e}$ and standard Gibbs energies of formation are reliably known.

The problem becomes more complex if the standard Gibbs energy of formation of the supposed representative ecospecies $\mathrm{R_e}$ is unknown. In this case, the element R is included in the "defect" list and then estimation methods or methods of thermodynamic forecasting are used [15–18].

In a number of cases, there arose a "conflict of data," e.g., the species themselves or the standard Gibbs energies of their formation, determined in [10] and [13], differed from each other such that it was difficult to select the representative species and the most probable Gibbs energy of formation of individual species. In this case, preference was given to more reliable data and the balances between the ecospecies were partially taken into account. These balances will be considered in more detail in a separate publication.

Estimation of the Function $\Delta_{\mathrm{f}}G^{\circ}_{298}$ of Some Probable Representative Ecospecies of Elements from the "Defect" List. As already noted, "defect" elements are elements, the function $\Delta_{\mathrm{f}}G^{\circ}_{298}$ of whose ecospecies is unknown; in this case, the standard exergy of an element cannot be calculated by formulas (6)–(8). Such species are formed by elements with different degrees of oxidation: Ir(4+), Mn(3+), Mn(4+), Rh(3+), Sn(4+), and Sb(+). The thermodynamic characteristics of species can be determined using the concept of "one-type" compounds [17, 18] or by the acid–base interaction of the oxides of elements [16]. We will illustrate the first method with the example of calculation of $\Delta_{\mathrm{f}}G^{\circ}_{298}\{\mathrm{H_3SbO_4^{\circ}}\}$ on the assumption that $\mathrm{H_3SbO_4^{\circ}}$ is the representative ecospecies of Sb(5+). This compound belongs in the one-type series $\mathrm{H_3PO_4^{\circ}}$–$\mathrm{H_3AsO_4^{\circ}}$–$\mathrm{H_3SbO_4^{\circ}}$, in which the value of $x_i = \Delta_{\mathrm{f}}H^{\circ}_{298}\{\mathrm{H_3RO_4^{\circ}}\}$ is characteristic of all of the terms of the series and the value of $y_i = \Delta_{\mathrm{f}}G^{\circ}_{298}\{\mathrm{H_3RO_4^{\circ}}\}$ is characteristic of only the two first terms [13]. According to [18], $\Delta_{\mathrm{f}}G^{\circ}_{298}\{\mathrm{H_3SbO_4^{\circ}}\}$ represents a linear coordinate y_3 if x_1, y_1, x_2, y_2, and x_3 are known, and it is determined (in kJ/mole) from the equation of a straight line defined by three points [10]:

$$\begin{aligned} y_3 &= [y_1(x_2 - x_3) - y_2(x_1 - x_3)]/(x_2 - x_1) = [-\,1142.65\,(-\,906.67 + 907.09)\; - \\ &-(-\,770.02)\,(-\,1288.34 + 907.09)]/(-\,906.67 + 1288.34) = -\,770.43\,, \end{aligned} \tag{10}$$

where the numerical values of the variables represent the corresponding thermodynamic characteristics of the compounds in the series $\mathrm{H_3PO_4^{\circ}}$–$\mathrm{H_3AsO_4^{\circ}}$–$\mathrm{H_3SbO_4^{\circ}}$.

The value of $\Delta_{\mathrm{f}}G^{\circ}_{298}\{\mathrm{H_3SbO_4^{\circ}}\}$ can be determined more correctly by linear extrapolation of the functions $\Delta_{\mathrm{ox}}G^{\circ}_{298}$ and $\Delta_{\mathrm{ox}}H^{\circ}_{298}$ called the "Gibbs ox-energy" and "Gibbs ox-enthalpy," respectively, in the above-indicated series of species $\mathrm{H_3RO_4^{\circ}}$ (R = P, As, Sb). These functions characterize the hydration of the corresponding half-pentoxides $\mathrm{RO_{2.5}}$ (or half a mole of $\mathrm{R_2O_5}$) according to the following stoichiometry:

$$[\mathrm{RO_{2.5}}] + \frac{3}{2}\{\mathrm{H_2O}\} = \{\mathrm{H_3RO_4^{\circ}}\}\,,$$

in accordance with which we obtained the expressions

$$\Delta_{\mathrm{ox}}G^{\circ}_{298}\{\mathrm{H_3RO_4^{\circ}}\} = \Delta_{\mathrm{f}}G^{\circ}_{298}\{\mathrm{H_3RO_4^{\circ}}\} - \Delta_{\mathrm{f}}G^{\circ}_{298}(\mathrm{RO_{2.5}}, \mathrm{c}) - \frac{3}{2}\Delta_{\mathrm{f}}G^{\circ}_{298}(\mathrm{H_2O}, \mathrm{liq})\,; \tag{11}$$

$$\Delta_{\mathrm{ox}}H^{\circ}_{298}\{\mathrm{H_3RO_4^{\circ}}\} = \Delta_{\mathrm{f}}H^{\circ}_{298}\{\mathrm{H_3RO_4^{\circ}}\} - \Delta_{\mathrm{f}}H^{\circ}_{298}(\mathrm{RO_{2.5}}, \mathrm{c}) - \frac{3}{2}\Delta_{\mathrm{f}}H^{\circ}_{298}(\mathrm{H_2O}, \mathrm{liq})\,. \tag{12}$$

Here, the abbreviations liq and c denote respectively the liquid and crystalline phases.

As was noted by V. A. Kireev [19], the properties of oxides determine the aprotic acid–base interaction of them in the process of formation of crystalline salts of oxygen-containing acids. Therefore, the ox-characteristics form the basis of the incremental method of determining the thermodynamic characteristics of the salts of these acids [16].

Using the ox-enthalpies of the species $H_3RO_4^{\circ}$ in Eq. (10) as the variables x_i and the Gibbs ox-exergies of the species $H_3RO_4^{\circ}$ as the variables y_i (i = 1, 2, 3), we will extrapolate the Gibbs ox-energies in the series of H_3RO_4 acids on the basis of linear correlation of them with the ox-enthalpies in the indicated series. Using the data of [14], we obtain (in kJ/mole)

$$x_1 = \Delta_{ox}H^{\circ}_{298}\left\{H_3PO_4^{\circ}\right\} = -\,113.6\,,\quad y_1 = \Delta_{ox}G^{\circ}_{298}\left\{H_3PO_4^{\circ}\right\} = -\,112.48\,;$$

$$x_2 = \Delta_{ox}H^{\circ}_{298}\left\{H_3AsO_4^{\circ}\right\} = -\,14.715\,,\quad y_2 = \Delta_{ox}G^{\circ}_{298}\left\{H_3AsO_4^{\circ}\right\} = -\,22.35\,;$$

$$x_3 = \Delta_{ox}H^{\circ}_{298}\left\{H_3SbO_4^{\circ}\right\} = 125.41\,,\quad y_3 = 14.21\,,$$

the last-mentioned value was extrapolated in accordance with (10). Substituting these values into (11), we obtain (in kJ/mole)

$$\Delta_f G^{\circ}_{298}\left\{H_3SbO_4^{\circ}\right\} = 14.21 - 432.37 = 1.5\cdot 237.1784 = -\,773.92\,.$$

The two independent methods of prediction have given close results, which points to its reliability. The desired quantity was estimated by averaging its values determined by these methods (in kJ/mole):

$$\Delta_f G^{\circ}_{298}\left\{H_3SbO_4^{\circ}\right\} = -\,772\,.$$

The method of estimating the acid–base interaction of oxides can be used more widely since it is based on the total series of salts [16] having a common (for all of the salts) anion or cation. Such series form more representative statistical samples and provide the obtaining of more reliable statistical estimates as compared to the estimates obtained in [18]. We used this method for estimating the functions $\Delta_f G^{\circ}_{298}$ of the dissolved hydroxocomplexes $\left\{R(OH)_d^{\circ}\right\}$ of the elements Mn, Ir, Rh, and Sn, or more specifically, for determining the values of $\Delta_f G^{\circ}_{298}\left\{Mn(OH)_3^{\circ}\right\}$, $\Delta_f G^{\circ}_{298}\left\{Mn(OH)_4^{\circ}\right\}$, $\Delta_f G^{\circ}_{298}\left\{Ir(OH)_4^{\circ}\right\}$, $\Delta_f G^{\circ}_{298}\left\{Rh(OH)_3^{\circ}\right\}$, and $\Delta_f G^{\circ}_{298}\left\{Sn(OH)_4^{\circ}\right\}$. Our supposition on the nature of the probable ecospecies of the indicated elements is based on the fact that these species are characteristic of elements containing amphoteric subacids or weakly basic hydroxides, as in the cases of Al, Si, and Zn and others. A complete set of values of $\Delta_f G^{\circ}_{298}\left\{R(OH)_d^{\circ}\right\}$ and $\Delta_f G^{\circ}_{298}\left\{RO_{d/2}, c\right\}$, which can be obtained using the data of [10, 13], includes 27 pairs of values that allow one to determine the values of $\Delta_{ox}G^{\circ}_{298}\left\{R(OH)_d^{\circ}\right\}$ characterizing of the acid–base interaction occurring in accordance with the stoichiometric equation analogous to (10) and the expression analogous to (11):

$$d\Delta_{ox}G^{\circ}_{298}\left\{R(OH)_d^{\circ}\right\} = \Delta_f G^{\circ}_{298}\left\{R(OH)_d^{\circ}\right\} - \Delta_f G^{\circ}_{298}\left\{RO_{d/2}, c\right\} - (d/2)\,\Delta_f G^{\circ}_{298}\left\{H_2O, liq\right\}. \tag{13}$$

It was established that, for the values of $\Delta_{ox}G^{\circ}_{298}$ from the above-indicated sample, the following statistical law with a Gaussian distribution of individual deviations of mole-equivalent values (in kJ/mole-eq. OH) is true:

$$\Delta_{ox}G^{\circ}_{298}\left\{R(OH)_d^{\circ}\right\} = 13.33.\pm 5.5\,. \tag{14}$$

As a result, we obtained the following values of the ecospecies being considered (hereinafter, all values are given in kJ/mole):

$$\Delta_f G^\circ_{298}\left\{\mathrm{Mn(OH)}_3^\circ\right\} = 13.33\cdot 3 - \frac{1}{2}879.87 - \frac{3}{2}237.1784 = -755.71\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Mn(OH)}_4^\circ\right\} = 13.33\cdot 4 - 466.66 - 2\cdot 237.1784 = -887.7\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Ir(OH)}_4^\circ\right\} = 13.33\cdot 4 - 188.4264 - 2\cdot 237.1784 = -609.5\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Rh(OH)}_3^\circ\right\} = 13.33\cdot 3 - \frac{1}{2}276.8427 - \frac{3}{2}237.1784 = -454.2\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Sn(OH)}_4^\circ\right\} = 13.33\cdot 4 - 519.9 - 2\cdot 237.1784 = -941\,.$$

For the molar values of $\Delta_{ox}G^\circ_{298}\left\{\mathrm{R(OH)}_d^\circ\right\}$, we obtained the dependence with a rectangular distribution of deviations

$$\Delta_{ox}G^\circ_{298}\left\{\mathrm{R(OH)}_d^\circ,\ \mathrm{aq}\right\} = 30.65 \pm 10.64\,, \tag{15}$$

from which it follows that

$$\Delta_f G^\circ_{298}\left\{\mathrm{Mn(OH)}_3^\circ\right\} = 30.65 - \frac{1}{2}879.87 - \frac{3}{2}237.1784 = -746.37\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Mn(OH)}_4^\circ\right\} = 30.65 - 466.66 - 2\cdot 237.1784 = -910.37\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Ir(OH)}_4^\circ\right\} = 30.65 - 188.4264 - 2\cdot 237.1784 = -632.13\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Rh(OH)}_3^\circ\right\} = 30.65 - \frac{1}{2}276.8427 - \frac{3}{2}237.1784 = -444.86\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Sn(OH)}_4^\circ\right\} = 30.65 - 519.9 - 2\cdot 237.1784 = -963.61\,.$$

Since the estimates obtained are very different, we will use the average values of the quantities being estimated, obtained from formulas (14) and (15):

$$\Delta_f G^\circ_{298}\left\{\mathrm{Mn(OH)}_3^\circ\right\} = (-755.71 - 746.37)/2 = -751.0\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Mn(OH)}_4^\circ\right\} = (-887.70 - 910.37)/2 = -899.0\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Ir(OH)}_4^\circ\right\} = (-609.5 - 632.13)/2 = -620.8\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Rh(OH)}_3^\circ\right\} = (-454.2 - 444.86)/2 = -449.5\,,$$

$$\Delta_f G^\circ_{298}\left\{\mathrm{Sn(OH)}_4^\circ\right\} = (-941.0 - 963.61)/2 = -952.3\,.$$

Based on the data obtained, we calculated the standard exergies of the elements presented in Table 3.

Discussion of Results. We will compare the Ocean-2 system with the previous Ocean-1 system [4] because other oceanic systems of standard reference exergies are absent in the literature. Identical calculation methods are used for both versions. These versions differ mainly in the constants Φ and Ψ involved in (6) because of the influence of pH, in accordance with (4), on the function $G_e(\mathrm{OH}^-)$ involved in both Φ, in accordance with (3), and in Ψ in accord-

TABLE 3. Preliminary 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 without Regard for the Equilibrium between the Species (Ocean-2 Version)

R	c_e(R), ng/kg	$\overset{\circ}{W}_{dis}$(R), kJ/mole-atom	R_e	$\Delta_f \overset{\circ}{G}_{298}(R_e)$, kJ/mole	$\overset{\circ}{W}$(R), kJ/mole-atom
1	2	3	4	5	6
Ac	$4 \cdot 10^{-8*)}$	107	$AcSO_4^+$	–1405.82	970.6
Ag	2	61.2	$AgCl_2^-$	–214.81	81.8
Al	30	51.0	$Al(OH)_3^\circ$	–1114.62	806.9
As	1205	44.4	$HAsO_4^{2-}$	–717.68	489.3
Au	0.02	74.1	$AuCl_2^-$	–151.17	31.1
B	$4.5 \cdot 10^{6}$	19.2	$B(OH)_3^\circ$	–968.64	629.1
Ba	$15 \cdot 10^{3}$	39.7	Ba^{2+}	–546.83	731.7
Be	0.21	60.6	$Be(OH)_2^\circ$	–777.81	599.2
Bi	0.03	73.2	BiO^+	–146.02	289.2
Br	$67 \cdot 10^{6}$	17.5	Br^-	–104.22	49.1
C	$27 \cdot 10^{6}$	$20.0^{**)}$	CO_2	–394.37	410.4
Ca	$412 \cdot 10^{6}$	11.3	Ca^{2+}	–552.76	709.3
Cd	70	52.5	$CdCl_2^\circ$	–354.97	285.9
Ce	0.7	64.4	$CeSO_4^+$	–1440.97	963.2
Cl	$19.35 \cdot 10^{9}$	1.44	Cl^-	–131.26	60.1
Co	1.2	61.0	Co^{2+}	–53.64	259.8
Cr	212	47.8	CrO_4^{2-}	–729.43	621.4
Cs	306	49.2	Cs^+	–291.56	413.4
Cu	150	49.2	$Cu(OH)_2^\circ$	–328.49	138.5
Dy	1.1	63.7	$DySO_4^+$	–1426.74	948.2
Er	1.2	63.6	$ErSO_4^+$	–1436.79	958.1
Eu	0.17	68.2	$EuSO_4^+$	–1343.9	869.8
F	$1.3 \cdot 10^{6}$	23.7	F^-	–279.99	231.1
Fe	30	52.9	$Fe(OH)_3^\circ$	–677.39	371.4
Ga	1.2	61.4	$Ga(OH)_4^-$	–1012.95	523.3
Gd	0.9	64.1	$GdSO_4^+$	–1425.32	947.2
Ge	5.5	57.7	$Ge(OH)_4^\circ$	–967.13	546.4
H	$1.1 \cdot 10^{11}$	0.047	H_2O	–237.18	117.6
Hf	0.07	70.8	$Hf(OH)_4^\circ$	–1495.78	1088.1
Hg	0.14	69.3	$HgCl_4^{2-}$	–448.86	129.8
Ho	0.36	66.5	$HoSO_4^+$	–1451.64	975.9
I	$58 \cdot 10^{3}$	36.1	IO_3^-	–125.94	81.5
In	0.01	74.5	$In(OH)_3^\circ$	–737.22	452.9
Ir	$1.3 \cdot 10^{-4}$	86.5	$Ir(OH)_4^\circ$	$(–620.8)^{***)}$	228.9
K	$399 \cdot 10^{6}$	10.8	K^+	–282.52	366.0
La	5.6	59.3	$LaCO_3^+$	–1258.13	977.2
Li	$180 \cdot 10^{3}$	26.1	Li^+	–292.29	391.0
Lu	0.23	67.8	$LuSO_4^+$	–1397.46	923.0
Mg	$1.28 \cdot 10^{9}$	7.24	Mg^{2+}	–457.31	609.8
Mn	20	53.8	$Mn(OH)_4^\circ$	(–889)	464.4
Mo	10^{4}	39.8	MoO_4^{2-}	–838.89	722.8

Continuation of Table 3

1	2	3	4	5	6
Na	$10.78 \cdot 10^9$	1.82	Na^+	–262.12	336.5
Nb	0.37	65.0	NbO_3^-	–950.19	934.6
Nd	3.3	60.7	$NdSO_4^+$	–1436.16	954.6
Ni	480	46.1	$NiCl_2^{\circ}$	–312.5	237.0
Os	0.009	76.0	$H_3OsO_6^-$	–732.62	369.2
P	$62 \cdot 10^3$	32.5	HPO_4^{2-}	–1089.26	848.9
Đà	$5 \cdot 10^{-5*)}$	89.4	Pa^{3+}	–426.52	733.7
Pb	2.7	62.1	$HPbO_2^-$	–400.95	268.2
Pd	0.06	69.9	$Pd(OH)_2^{\circ}$	–287.02	117.7
Pr	0.7	64.5	$PrSO_4^+$	–1444.32	966.5
Pt	0.05	71.8	$Pt(OH)_2^{\circ}$	–268.98	101.6
Ra	$1.3 \cdot 10^{-4}$	86.9	Ra^{2+}	–556.63	788.8
Rb	$120 \cdot 10^3$	33.3	Rb^+	–283.55	389.5
Re	7.8	59.2	ReO_4^-	–711.47	687.4
Rh	0.08	69.1	$Rh(OH)_3^{\circ}$	(–449.5)	159.8
Ru	0.002	78.2	RuO_4^-	–242.67	237.5
S	$898 \cdot 10^6$	8.87	SO_4^{2-}	–743.83	596.7
Sb	200	50.1	$H_3SbO_4^{\circ}$	(–772)	460.6
Sc	0.7	61.6	$ScHPO_4^+$	–1727.99	885.3
Se	155	49.6	SeO_4^{2-}	–441.412	335.2
Si	$2.8 \cdot 10^6$	22.8	$Si(OH)_4^{\circ}$	–1309.88	854.3
Sm	0.57	65.1	$SmSO_4^+$	–1428.0	950.9
Sn	0.5	64.9	$Sn(OH)_4^{\circ}$	(–952.3)	538.8
Sr	$7.8 \cdot 10^6$	23.1	Sr^{2+}	–563.95	732.2
Ta	0.03	72.6	$HTaO_3^{\circ}$	–1127.6	1075.6
Tb	0.17	68.3	$TbSO_4^+$	–1430.13	956.2
Te	0.07	69.9	$HTeO_3^-$	–452.29	324.7
Th	0.02	74.5	$Th(OH)_2^{2+}$	–1163.99	1144.5
Ti	6.5	56.3	$Ti(OH)_4^{\circ}$	–1318.38	896.2
Tl	13	58.1	$TlCl^{\circ}$	–167.38	164.7
Tm	0.2	68.0	$TmSO_4^+$	–1435.95	961.7
U	$3.2 \cdot 10^3$	44.9	$UO_2(CO_3)_2^{2-}$	–2102.17	1170.8
V	$2 \cdot 10^3$	42.2	$H_2VO_4^-$	–1020.9	746.0
W	10	58.5	WO_4^{2-}	–931.36	834.0
Y	17	55.4	YSO_4^+	–1453.94	967.1
Yb	1.2	63.6	$YbSO_4^+$	–1410.0	931.4
Zn	350	47.2	$ZnCl^+$	280.62	339.6
Zr	15	55.8	$Zr(OH)_4^{\circ}$	–1466.91	1044.3

Note. $^{*)}$Data of [11]; $^{**)}$values of elements in air; $^{***)}$parenthetical data representing extrapolated values.

ance with (7), which allows the conclusion that the consideration of pH in calculations of the exergies of elements in oceanic systems is of paramount importance. The Ocean-2 system proposed in the present work is an approximation that makes it possible to obtain more exact values of the exergies of elements in a medium that is most close to the actual oceanic medium; therefore, this system can be recommended for engineering, technological, and other applications that do not pretend to a very high accuracy. The main fields where the exergic method can be used are considered in [6].

Of interest is comparison of the Ocean-2 system of standard reference exergies with the widely used lithospheric-heterophase system [7, 8]. Here, we will make only general comments. Even though the Ocean-2 oceanic system differs radically from the lithospheric-heterophase system in reference substances, the difference between them in numerical values of the standard exergies of elements is not so large. It was found that in 80 cases of 100, they differ by not more than 40 kJ/mole-atom. Therefore, we believe that the differences between the oceanic and lithospheric-heterophase systems can be further decreased; however, this problem has yet to be investigated to a sufficient extent. Evidently, to further improve the exergies of elements determined in the Ocean-2 system, it is necessary to consider the equilibrium transformations of their species. This problem will be the subject of a further investigation.

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NOTATION

$a_{\rm H}$, $a_{\rm OH}$, $a_{\rm H_2O}$, $a(A_j)$, thermodynamic activity of the species H^+, OH^-, and H_2O and of the arbitrary species A_j respectively; C, molar concentration of a species, kmole/m^3; $C_{\rm e}(R)$, molar concentration of the element R (kmole/m^3); $c_{\rm e}(R)$, mass concentration of the element R in the oceanic medium, ng/kg; d, number of hydrooxygroups in the formula of a hydroxide; f, number of oxygroups in the formula of an ecospecies; G, molar Gibbs energy of formation of a species; $\Delta_{\rm f}G^{\circ}_{298}$ and $\Delta_{\rm ox}G^{\circ}_{298}$, standard reference Gibbs energy of formation of a species from elements and oxides, kJ/mole; $\Delta_{\rm f}H^{\circ}_{298}$ and $\Delta_{\rm ox}H^{\circ}_{298}$, standard reference heat of formation of a species from elements and oxides, kJ/mole; $K_{\rm w}$, ionic product of water, Mmole^2/m^6; L^-, arbitrary ligand in the formula of an ecospecies; $M(R)$, molar mass (atomic weight) of the element R; n, number of ions or groups of ligands L in the form of ecospecies; P, total pressure or partial pressure, Pa; R, arbitrary chemical element; $R_{\rm e}$ and $\{RO_fL_n\}^k_{\rm e}$, nonstoichiometric and stoichiometric designations of the ecospecies of the element R; R, universal gas constant; S, salinity, g/kg or ‰ (pro mille); t and T, temperature, $^{\rm o}$C and K; W, molar exergies of the element R, kJ/mole-atom; $W^{\circ}_{\rm ch}(R)$, chemical exergy of the element R, kJ/mole-atom; $W^{\circ}_{\rm dis}(R)$, work of dilution of the ecospecies of the element R from the standard concentration, pressure, or activity to the environmental ones, kJ/mole-atom; w, specific exergy of the element R, MJ/kg; x_1, x_2, ... and y_1, y_2, ..., first, second, and so forth values of the variables x and y; $z(z_j)$, degree of oxidation of the element R in an ecospecies (jth ecospecies); Φ, absolute value of the molar Gibbs energy of a hydrated electron, kJ/mole; Ψ, absolute value of the molar Gibbs energy of oxolation, kJ/mole. Subscripts: e, environment, reference medium, ecostate; f, reaction of formation of species of elements; ox, formation of species from oxides; ch, chemical; dis, dissolution; w, water. Superscripts: k, formal charge of an ecospecies; °, neutral charge of a species or its standard state depending on the pressure or concentration.

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