NEW SYSTEM OF STANDARD EXERGIES OF CHEMICAL ELEMENTS. I. STANDARD EXERGIES OF IONOGEN ELEMENTS

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A system of standard exergies of chemical elements and individual substances is proposed that is based on the choice of the aqueous phase of the World Ocean — "sea water" — as an environmental niche and the choice of simple (one-element) cations and anions existing in it — with account for their concentrations — as reference substances for their constituting ionogen elements. Standard exergies of ionogen elements are calculated.

According to the main postulate of the concept of exergy [1], the reference level for determination of the exergies of environmental substances (reference substances, environment components) is their state (chemical form and concentration) in the environment, and the state of all other substances (nonenvironmental substances) is equilibrium relative to the environment as a whole or to one of its niches, i.e., the atmosphere, hydrosphere, or lithosphere, and can be calculated by the formula

$$W = H - H_e - T_e (S - S_e).$$ (1)

Since direct use of formula (1) encounters some difficulties due to the absence of data on H_e and S_e, it is useful to calculate beforehand the standard exergies of chemical elements. If they are known, then the exergy of any compound described conventionally by the formula $A_a B_b X_x Y_y$ can be calculated as

$$W (A_a B_b X_x Y_y) = aW (A) + bW (B) + xW (X) + yW (Y) + \Delta_f G (A_a B_b X_x Y_y)\}.$$ (2)

The standard exergy W^o of any substance is the exergy of one mole of the substance under standard (in the thermodynamic sense) conditions of its existence, i.e., for the standard phase state and at the standard temperature T^o (298.15 K) and pressure P^o (1 atm, $1.01325 \cdot 10^5$ Pa) with formal replacement of H and S in (1) by their standard values H^o and S^o. The normal exergy W_n of a substance is the molar exergy that meets the condition that the environmental substance (the reference substance) is under standard conditions, i.e., at the standard temperature and pressure and the standard concentration C^o of the reference substance in the liquid phase, equal to 1 M (1 mole/liter, 1 kmole/m^3). In going from normal to standard exergies it is necessary to add to the former the exergy of dilution of the reference substance, provided that the concentration of the reference substance changes from the standard one, equal to 1 M, to the environmental one, equal to C_e:

$$W_{dil} = RT_e \ln (C^o/C_e) = - RT_e \ln C_e.$$ (3)

For reference substances, foremost H_2O, characterized by the thermodynamic activity in sea water a_e, the exergy of dilution is determined according to the formula

$$W_{dil} = - RT_e \ln a_e.$$ (4)

If a reference substance is present in the atmosphere and is characterized by the partial pressure P_e, then the exergy of its dilution coincides with the exergy of isothermal gas expansion from the standard P^o to the environmental P_e pressure. It should be noted that when pressures are expressed in fractions of the standard atmospheric pressure, i.e., in relative units coinciding numerically with the pressure in physical atmospheres, the expressions become considerably simplified. With regard for this, henceforth gas and vapor pressures will be expressed in atmospheres (atm), and for the exergy of dilution of a gas we obtain the following expression

$$W_{dil} = RT_e \ln (P^o/P_e) = - RT_e \ln P_e . \tag{5}$$

Owing to the monograph [1], the Szargut system of standard exergies of substances, based on consideration of two ecological niches (spheres), namely, the atmosphere and the lithosphere, has become internationally known. The World Ocean in [1] as an environmental niche was not taken into consideration at first. In [2], this condition was corrected, though, in our opinion, insufficiently. A more decisive attempt was undertaken by V. S. Stepanov [3]; however it should be considered unsuccessful because of serious methodological errors, discussed by the present authors previously [4]. Of definite interest is the work by H. Kameyama [5], where the water activity of water is assumed to be equal to 0.9849, which is consistent with its value in Ocean water. Unfortunately, in that work some reference substances are adopted arbitrarily, which violates the integrity of the entire system of exergies. The present authors develop the approach they reported previously [4] but with a more accurate account of the thermodynamic characteristics of H_2O and Ocean water. Key importance in a system of standard exergies of chemical elements belongs to water, oxygen, carbon dioxide, and hydrogen. The standard values of the first three of them are equal to the isothermal work of expansion (dilution) from the standard to the environmental state according to (3)-(5). Thus for water in the liquid state we obtain according to (4) and with account for as activity $a_e = 0.9849$ in Ocean water

$$W^o (H_2O , liq) = - 8.31434 \cdot 298.15 \ln 0.9849 = 37.7 \ \text{J/mole} .$$

To calculate the standard exergy of water vapor, we employ data on the pressure of saturated H_2O vapor at 298.15 K [16], equal to 0.0313 atm. With regard for the activity of H_2O in sea water we obtain the equilibrium pressure of H_2O vapor above sea water as

$$P_e (H_2O) = 0.0313 \cdot 0.9849 = 0.030828 .$$

Hence according to (5) the standard exergy of water vapor is equal to

$$W^o (H_2O , g) = - 8.31434 \cdot 298.15 \ln 0.030828 = 8625 \ \text{J/mole} .$$

The total pressure of the other, besides H_2O, components of the atmosphere (the "dry" components) is

$$f = 1 - 0.030828 = 0.969172 .$$

After multiplying this value by the pressures of the dry-air components, we obtain the pressures of the latter in the moist environmental atmosphere. Thus, the O_2 pressure in dry air is 0.2093 atm, and after recalculating it for the moist atmosphere it turns out to be

$$P_e (O_2) = 0.969172 \cdot 0.2093 = 0.20284783 .$$

Now we use this value to calculate the standard exergy of oxygen according to (5):

$$W^o (O_2) = - 8.31434 \cdot 298.15 \ln 0.20284783 = 3954.62 \ \text{J/mole} .$$

Similarly, we calculate the standard exergies of the other components of the atmosphere, given in Table 1.

TABLE 1. Standard Exergies of Components of the Environmental Atmosphere

Component	P_e in dry air, %	W^o, J/mole	Component	P_e in dry air, %	W^o, J/mole
N_2	78.1	690.36	He	$5 \cdot 10^{-4}$	30,335.54
O_2	20.93	3854.62	Ne	$1.8 \cdot 10^{-3}$	27,160.29
Ar	0.9325	11,666.72	Kr	$1 \cdot 10^{-4}$	34,325.12
CO_2	0.03	20,185.95	Xe	$9 \cdot 10^{-6}$	40,294.36

Using the standard exergy $W^o(CO_2)$, equal, according to Table 1, to 20,185.95 J/mole, as well as $W^o(O_2)$ = 3954.62 J/mole and $\Delta_f G^o(CO_2, g, 298.15 K)$ = −394,374.34 J/mole [7], we calculate the standard exergy of carbon (graphite), J/mole, by formula (2):

$$W^o (C, graphite) = 20,185.95 - (- 394,374.34) - 3954.62 = 410,605.67 .$$

To determine the standard exergy of hydrogen, we conduct (at an environmental temperature and pressure coinciding with the standard values) the reaction of H_2 devaluation in a reversible fuel cell with the participation of two environmental media, namely, air and sea water, in which the exergies of the reference substances O_2 and H_2O are equal, by definition, to zero. The work done in this isobaric and isothermal process, equal to the standard exergy of hydrogen, is also equal to the change in the Gibbs energy of the reaction of H_2 and O_2 with formation of H_2O or to the reciprocal change in the Gibbs energy of the reverse reaction, namely, electrolysis of water in a reversibly (in an equilibrium mode) operating electrolytic cell. This process is a combination (stoichiometric sum) of two electrode half-reactions, namely, the cathode half-reaction of hydrogen formation and the anode half-reaction of oxygen formation, which are characterized by their equilibrium electrode potentials. In this approach, the exergy of hydrogen, expressed in volts (V), more precisely in electron-volt/mole-equivalent (eV/mole-eq.), is equal to the difference of the electric potentials of the cathode (the hydrogen electrode) and the anode (the air electrode). By multiplying the obtained value by the Faraday constant 96,487, we obtain the sought quantity in J/mole-eq., and next by taking into account the number of electrons in a half-reaction − in units of J/mole. The same procedure can be adopted for calculation of the standard exergies of any chemical element R_m, where m is the number of atoms in the chemical formula of the element substance existing in sea water as a simple ion R^z, by using reference data on the normal electrode potentials of the chemical elements [6] and the air electrode. In view of the paramount importance of the latter we perform its calculation.

The stoichiometric equation of the anode process on the air electrode is

$$O_2 = 4 \left\{ OH^-, aq \right\} - 2 \left\{ H_2O, liq \right\} - 4e^- .$$
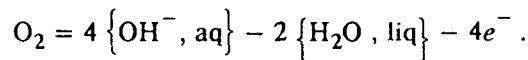
The extended version of the Nernst equation for 298.15 K is

$$\varphi (O_2/OH^-) = 0.4011329 + 0.059157455 \log \left\{ \sqrt[4]{P_e (O_2)} \sqrt{a_e (H_2O)} / a_e (OH^-) \right\} . \tag{6}$$

The activities of water, hydroxyl ions, and hydrogen are related by the equations of ionic equilibrium and balance of H^+ and OH^- ions in water as

$$a_e (H^+) a_e (OH^-) / a_e (H_2O) = K_w = 1.01048 \cdot 10^{-14} ,$$

$$a_e (OH^-) = a_e (H^+) = \sqrt{K_w a_e (H_2O)} . \tag{7}$$

By substituting (7) in (6), we obtain the ordinary Nernst equation [6]

TABLE 2. Standard Exergies of Chemical Elements Presumably Existing in Sea Water in the Form of One-Element Ions

Element, R_m	z	$-\Delta_f G^\circ(R^z, \text{aq.})$, J/mole	C_e, g/liter	$W^\circ(R_m)$, J/mole
Li	+1	292,628.96	$2 \cdot 10^{-4}$	396,203
Na	+1	262,219.64	10.5	341,746.5
K	+1	282,658.48	0.38943	371,742.3
Rb	+1	283,842.56	$1.2 \cdot 10^{-4}$	394,905.25
Cs	+1	291,750.32	$5 \cdot 10^{-7}$	417,495.15
Cu	+2	-65,270.4	$3 \cdot 10^{-6}$	131,861.85
Ag	+1	-77,106.94	$3 \cdot 10^{-7}$	49,386.8
Be	+2	381,162.4	$8 \cdot 10^{-10}$	594,566
Mg	+2	455,261.04	1.35	617,742.55
Ca	+2	552,706.4	0.41	719,381.85
Sr	+2	571,450.72	$1.363 \cdot 10^{-2}$	748,503.1
Ba	+2	547,518.24	$3 \cdot 10^{-5}$	740,852.75
Ra	+2	556,695.11	$1 \cdot 10^{-13}$	799,611.25
Zn	+2	147,193.12	$1 \cdot 10^{-5}$	341,411.45
Cd	+2	77,864.24	$1.1 \cdot 10^{-7}$	284,605.25
Hg	+2	-164,431.2	$3 \cdot 10^{-8}$	46,966.26
Al	+3	491,996.56	$1 \cdot 10^{-5}$	761,678.46
Ga	+3	87,864	$3 \cdot 10^{-8}$	374,299.66
Tl	+1	32,426	$1 \cdot 10^{-8}$	168,935.66
Sc	+3	601,240.8	$4 \cdot 10^{-8}$	885,875.76
Y	+3	686,594.44	$3 \cdot 10^{-7}$	967,924.96
La	+3	686,176	$3 \cdot 10^{-7}$	968,612.66
Ce	+3	675,716	$4 \cdot 10^{-7}$	957,461.06
Th	+4	723,832	$7 \cdot 10^{-7}$	1,084,484.5
Pb	+2	24,392.72	$1 \cdot 10^{-7}$	232,885.85
Bi	+3	-91,838.8	$2 \cdot 10^{-7}$	192,615.46
Cr	+3	203,928.16	$5 \cdot 10^{-8}$	488,370.66
F$_2$	-1	279,993.3	$1.3 \cdot 10^{-3}$	452,213.8
Cl$_2$	-1	131,260.44	19.0	110,297.42
Br$_2$	-1	104,223.44	0.065	88,401.75
J$_2$	-1	51,588.72	$6 \cdot 10^{-5}$	20,070.4
Mn	+2	229,952.64	$2 \cdot 10^{-6}$	427,729.15
Pe	+3	17,865.68	$1 \cdot 10^{-5}$	289,351.21
Co	+2	56,107.44	$5 \cdot 10^{-7}$	257,494.25
Ni	+2	45,103.52	$2 \cdot 10^{-6}$	243,043.65

$$\varphi \, (O_2/OH^-) = 0.4011329 + 0.059157455 \log \left\{ \sqrt[4]{P_c \, (O_2)} \, \sqrt{K_w} \right\} . \tag{8}$$

The identity of Eqs. (6) and (8) means that the potential of the air electrode in sea water is equal to its potential in pure water and, consequently, it does not depend on the presence of salts in the water that do not change its pH. After substituting the numerical values of $P_c(O_2)$ and K_w, equal to 0.20284788 and $1.01048 \cdot 10^{-14}$, respectively, we obtain

$$\varphi \, (O_2/OH^-) = + \, 0.80485465 \, B . \tag{9}$$

Multiplication of the obtained value of (9) by the Faraday constant gives (in J/mole-eq.)

$$\Phi = - \, 77658.0 . \tag{10}$$

This constant allows calculation of the exergies of ionogen elements existing in sea water in the form of simple ions by using reference data [7] on the standard Gibbs energies of the ions R^z ions in aqueous solutions $\Delta_f G^o(R^z$, aq., 298.15 K). With due regard for this we obtain the following formula for calculation of the normal exergies of chemical elements forming simple ions in sea water:

$$W_n \, (R_m) - m \, [\Delta_f G^0 \, (R_z, \, \text{aq}, \, 298.15 \, K) + z\Phi] . \tag{11}$$

To calculate the standard exergies of ionogen elements it is necessary to add to the values obtained by (11) the work of dilution of aqueous solutions of the ions from the standard to the environmental concentrations according to (3). In the special case of calculation of the exergy of hydrogen we take into consideration in the work of dilution of the hydrogen ion the activity of the H^+ ion, which after substituting the value of $a_e(H^+)$ from (7) allows us to represent the Nernst formula for a hydrogen electrode in the form

$$\varphi \, (H_2/H^+) = 0 - 0.059157455 \log a_e \, (H^+) . \tag{12}$$

As a result, we obtain a formula for calculation of the standard exergies of ionogen elements:

$$W^o \, (R_m) = W_n \, (R_m) - m \, 8.31434 \cdot 298.15 \ln C_e . \tag{13}$$

Now we consider the applicability of suggested formulas (11)-(13) for hydrogen, aluminum, and chlorine, taken as examples, by using data on the content of the elements in sea water [8]:

H_2: $\Delta G^o(H^+$, aq., 298.15 K) = 0 J/mole, $a_e(H^+)$ = $(1.0052263 \cdot 10^{-7} \cdot \sqrt{0.9849})$ = $0.997608 \cdot 10^{-7}$; $W_n(H_2)$ = $-2 \cdot [0 + 1(-77,658.1)]$ = 155,316.0 J/mole, $W^o(H_2)$ = 155,316.0 $- \, 2 \cdot 8.31434 \cdot 298.15 \ln (0.997608 \cdot 10^{-7})$ = 235,238.8 J/mole. This quantity can be checked by formula (2): $W^o(H_2)$ = $W^o(H_2O) - (1/2)(W^o(O_2) - \Delta_f G^o(H_2O$, liq., 298.15 K) = 37.7 $- \, 3954.62/2 - (-237,178.4)$ = 235,238.8 J/mole, which practically coincides with the previous result.

Al: $\Delta_f G^o(Al^{+3}$, aq., 298.15 K) = $-491,996.56$ J/mole, the aluminum concentration in sea water is 0.01 mg/liter or $3.70645 \cdot 10^{-7}$ mole/liter, $W_n(Al)$ = $-[-491,996.56 + 3(-77,658.0)]$ = 724,970.6 J/mole, the exergy of dilution of Al^{+3} is $W_{dil}(Al^{+3})$ = $-8.31434 \cdot 298.15 \ln (3.70645 \cdot 10^{-7})$ = 36,707.9 J/mole, the standard exergy is $W^o(Al)$ = 724,970.6 + 36,707.9 = 761,678.46 J/mole.

Cl_2: $\Delta_f G^o(Cl^-$, aq., 298.15 K) = $-131,260.44$ J/mole, the chlorine ion concentration in sea water is 19 g/liter [8] or 0.53591 M. The normal exergy is $W_n(Cl_2)$ = $-2 \cdot [-131,260.44 - (-77,658.0)]$ = 107,204.88 J/mole, the exergy of dilution of one mole of the Cl-ion is W_{dil} = $-8.31434 \cdot 298.15 \ln (0.53591)$ = 1546.27 J/mole, the standard exergy is $W^o(Cl_2)$ = 107,204.88 + $2 \cdot 1546.27$ = 110,297.42 J/mole.

Results of our calculations are given in Table 2.

Methods of calculation of the standard exergies of elements existing in sea water in equilibrium with the atmosphere in the form of complex ions will be discussed in the next publication.

NOTATION

W, molar exergy of a substance at arbitrary temperature, pressure, and concentration, J/mole; W_{dil}, isothermal molar exergy of dilution of a substance from the standard to the environmental concentration; H, molar enthalpy of a substance at arbitrary temperature, pressure, and concentration, J/mole; H_e, environmental molar enthalpy of a substance; H^o, standard molar enthalpy of a substance; S, molar entropy of a substance at arbitrary temperature, pressure, and concentration, J/(mole·K); S_e, environmental molar entropy of a substance; S^o, standard molar entropy of a substance; T_e, environmental temperature (298.15 K by agreement); T^o, standard temperature, 298.15 K; P^o, standard pressure, 1 atm (1.01325·10^5 Pa); P_e, relative partial pressure of the reference substance; C^o, standard concentration of the reference substance, 1 M; C_e, environmental concentration of the reference substance, mole/liter, kmole/m^3; R, universal gas constant, J/(mole·K); R_m, formula of the element substance in the standard state; R^z, form of the ion of the element R_m in sea water (the environment); z, formal ion charge (the number with the sign "+" for a cation and "−" for an anion); $\Delta_f G(A_a B_b X_x Y_y)$, Gibbs-energy change upon formation of the substance $A_a B_b X_x Y_y$, J/mole; f, total relative pressure of the "dry" elements of the atmosphere; a_e, thermodynamic activity of the reference substance; $\varphi(O_2/OH^-)$, potential of the oxygen ("air") electrode; $\varphi(H_2/H^+)$, potential of the hydrogen electrode; K_w, ion production of water; φ, work of the air electrode, J/mole-eq.

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