

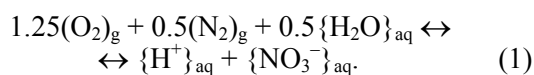
УДК 66.012–52.063

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IMPROVEMENT OF SYSTEM EXERGY OF CHEMICAL ELEMENTS

The article focuses on the fact that the existing systems standard exergies chemical elements are not quite correct thermodynamically, the indicators that are negative values exergies nitrate salts and some other substances. The reason is that the three dominant components of the environment oxygen and nitrogen in the atmosphere and water in the ocean have thermodynamic probability of chemical interaction to form nitrate ion in the ocean. In this paper calculated the equilibrium contents of O₂ and N₂ in the atmosphere and the equilibrium concentration of NO₃⁻-ion in the ocean water, as calculated molar exergies O₂ and N₂ and the air. Shown the air is the holder of the positive exergy and workability, and should not be regarded in exergy applications as "gift resources".

Introduction. Known systems standard exergies of chemical elements published in [1–11] does not account for the thermodynamic probability the chemical interaction between the three dominating species of the Environment – N₂ and O₂ in the atmosphere and H₂O in the ocean. L. Sillen was the first who alarmed in [12] the possibility of reaction (1) in the ocean



Attempts to examine the reaction between O₂ and N₂ on the earth surface and deep in the earth's crust were taken by Ahrendts in [13], but the proposals for revision the existing systems standard exergies of chemical elements was not followed, as this was contrary to the dogma which strongly supported by "gurus" in exergy paradigm J.Szargut [1–5], saying that exergy of each dominating component in the existing Environment equals zero ('reference level', 'datum') regardless to the state thermodynamic equilibrium of the components in the Environment.

Ahrendts noted that in absence the equilibrium state of components in the Environment their exergies and workability should be considered positive values. Therefore, the subsequent revision standard exergies of O₂ and N₂, and then standard exergies of the other elements depending upon exergies of O₂ and N₂ through a chain of relationships in their calculation scheme, is a challenge to Exergy adepts required by the logic of exergy paradigm.

To accept the idea of such a revision the systems standard exergies of chemical elements, some international scientific consensus is necessary, the achievement of which, we hope, is a matter of time.

Taking this into account, an objective of this work is compute the equilibrium parameters of reaction (1) at different pH and on this basis recalculate existing values the standard exergies of O₂ and N₂.

Planetary data. By analogy with the reactions of CO₂ in the hydrosphere, reaction (1) can be called the sequestration reaction of nitrogen with

oxygen in sea water, but its more common names are the reaction of nitrogen fixation or nitrification reaction. It is believed that at temperatures of 300 K the actual conditions reaction (1) is not observed, and hence, our discussion only characterizes the thermodynamic probability the reaction (1) in the absence other possible accompanying reactions.

The factors accompanying the reaction (1) may include the impact of possible catalysts and neutralizing H⁺ ion by alkali components of ocean water – carbonates, bicarbonates and hydroxides of calcium and magnesium dissolved in the ocean water, also considering a balance of the contacting with the aqueous medium solid calcium and magnesium carbonates composed sediments and reefs.

In addition to the kinetic limitations of the reaction (1) at low temperatures, in the direction of the reverse reaction (1) in the ocean environment is very actively proceed denitrification because of presence the reducing substances - hydrocarbons and other organic substances, phytoplankton and other micro-organisms in the ocean

Take values of global masses of environment compartments, according to [14]:

- 1) The mass of the ocean $m(\text{oc.}) = 1400 \cdot 10^{18} \text{ kg}$
- 2) The mass of the atmosphere $m(\text{atm.}) = 5.3 \cdot 10^{18} \text{ kg}$:

Main part. *Calculation of the equilibrium parameters of the reaction (1).* The composition of the ocean water is very complex [14], and it includes natural ever-present in the ocean species formed by all non-radioactive elements, species formed by some radioactive chemical elements and their decay products. The composition of the ocean water is the result of interaction of the ocean water layer, the average thickness of which is 3.8 km, with the mineral tectonically mobile ocean floor, characterized by almost continuous volcanic gases and secretions substances of lava flows into the ocean.

To perform calculations, equilibria of chemical and phase interactions in the global mega atmosphere – ocean system are modeled by chemical reactor, using a closed physical-chemical sys-

tem with the same mass ratio as the ratio of the masses in the considered above global mega atmosphere-ocean system, at standard temperature $T = 298.15$ K and at standard pressure $P = 101.325$ kPa, composed of 1 kmol air and a proportionate amount of ocean water.

Initial data for calculation of the equilibrium reaction (1). The composition of humid atmosphere (mole fractions, %) [11]: $O_2 - 20.54$, $N_2 - 76.34$, $Ar - 0.92$, $CO_2 - 0.0335$, $H_2O - 2.17$.

The molar mass of the dry atmosphere [14] is 28.966 kg / kmole, the molar mass of humid atmosphere -

$$28.966 \cdot (1 - 0.0217) + 18.015 \cdot 0.0217 = 28.73 \text{ kg/kmole.}$$

The specific volume of the oceanic water (m^3), interacting with 1 kmole of the atmospheric air

$$v = 28.73 \cdot 1400 \cdot 10^{18} / (1.023337 \times 5.3 \cdot 10^{18}) = 7.416, \text{ m}^3/\text{kmole.}$$

Thermochemical characteristics reactants of the reaction (1) [15]:

- the standard Gibbs energy formation reactants of the reaction (1) $\text{kJ} \cdot \text{mole}^{-1}$: $\Delta_f G^\circ(O_2, \text{g}, 298.15 \text{ K}) = 0$, $\Delta_f G^\circ(N_2, \text{g}, 298.15 \text{ K}) = 0$, $\Delta_f G^\circ(H^+, \text{aq.}, 298.15 \text{ K}) = 0$, $\Delta_f G^\circ(OH^-, \text{aq.}, 298.15 \text{ K}) = -157.224$, $\Delta_f G^\circ(H_2O, \text{l}, 298.15 \text{ K}) = -237.129$, $\Delta_f G^\circ(NO_3^-, \text{aq.}, 298.15 \text{ K}) = -108.74$;

- the activity coefficients of the reaction reactants (1) into the ocean water with a salinity standard 35‰ [11, 15, 16]: $\gamma(H^+) = 0.723$, $\gamma(OH^-) = 0.625$, $\gamma(NO_3^-) = 0.62$, $\gamma(H_2O) = 0.98$.

Additional characteristics of ocean water:

- 1) acidity $\text{pH} = 8.12$;
- 2) the average density = 1023.337 kg/m^3 ;
- 3) the concentration of nitrate ion $C(NO_3^-) = 3 \cdot 10^{-5} \text{ M}$ (or kmole/m^3) [14].

Mode options of reaction (1). In the calculations of equilibrium states in the contact zone of environment atmosphere - ocean, the regimes of the following options for the reaction (1) were considered (1):

Option 1 - without additional concentration limits;

Option 2 - with a predetermined indicator of acidity $\text{pH} = 8.12$, according to [11].

Calculations of the reaction equilibria (1). Calculations are made for 1 kmole of product NO_3^- prepared by means of reaction (1) applying the following equation of stoichiometric balance Gibbs energy for reaction (1) [9, 10]:

$$-1.25 \cdot G(O_2) - 0.5 \cdot G(N_2) - 0.5 \cdot G(H_2O) + G(H^+) + G(NO_3^-) = 0, \quad (2)$$

where: $G(O_2)$, $G(N_2)$, $G(H_2O)$, $G(H^+)$, $G(NO_3^-)$ - analytical or numerical values the chemical potentials (the Gibbs partial molar energies) of species O_2

and N_2 in the atmosphere, or species H_2O , H^+ , NO_3^- in the ocean --all values in the equilibrium state of reaction (1). Express the above thermodynamic constants using molar fractions reactants from mass balance of reaction (1) N , $\text{kJ} \cdot \text{mole}^{-1}$:

$$G(O_2) = \Delta_f G^\circ(O_2, \text{g}, 298.15 \text{ K}) + RT \cdot \ln N(O_2) = 0 + 2.4789 \cdot \ln((0.2054 - 1.25 \cdot y) / (1 - 1.75 \cdot y)), \quad (3)$$

$$G(N_2) = \Delta_f G^\circ(N_2, \text{g}, 298.15 \text{ K}) + RT \cdot \ln N(N_2) = 0 + 2.4789 \cdot \ln((0.7634 - 0.5 \cdot y) / (1 - 1.75 \cdot y)), \quad (4)$$

$$G(H_2O) = \Delta_f G^\circ(H_2O, \text{l}, 298.15 \text{ K}) + RT \cdot \ln a(H_2O) = -237.129 + 2.4789 \cdot \ln 0.98 = -237.179, \quad (5)$$

$$G(H^+) = \Delta_f G^\circ(H^+, \text{aq.}, 298.15 \text{ K}) + RT \cdot \ln a(H^+) = 0 + 2.4789 \cdot \ln(y \cdot \gamma(H^+) / v + \exp_{10}(-\text{pH})) = 2.4789 \cdot ((\ln(y \cdot 0.723 / 7.416) + \exp_{10}(-8.12))) = -5.7709 + 2.4789 \cdot \ln(y + 7.7809 \cdot 10^{-8}), \quad (6)$$

$$G(NO_3^-) = \Delta_f G^\circ(NO_3^-, \text{aq.}, 298.15 \text{ K}) + RT \cdot \ln a(NO_3^-) = -108.74 + 2.478926 \cdot \ln(y \cdot \gamma(NO_3^-) / v) = -114.89189 + 2.478926 \cdot \ln y. \quad (7)$$

The results of substituting the expressions (3)-(7) in (2):

$$-1.25 \cdot 2.4789 \cdot \ln((0.2054 - 1.25 \cdot y) / (1 - 1.75 \cdot y)) - 0.5 \cdot 2.4789 \cdot \ln((0.7634 - 0.5 \cdot y) / (1 - 1.75 \cdot y)) - 0.5 \cdot (-237.179) - 5.7709 + 2.4789 \cdot \ln(y + 7.781 \cdot 10^{-8}) - 114.8919 + 2.4789 \cdot \ln y = 0, \quad (8)$$

$$-1.25 \cdot \ln((0.2054 - 1.25 \cdot y) / (1 - 1.75 \cdot y)) - 0.5 \cdot \ln((0.7634 - 0.5 \cdot y) / (1 - 1.75 \cdot y)) + \ln(y + 7.781 \cdot 10^{-8}) + \ln y = 0.83637. \quad (9)$$

Transform (9) into the equation of "law of mass action for equilibria":

$$y \cdot (y + 7.781 \cdot 10^{-8}) \cdot (1 - 1.75 \cdot y)^{1.75} / ((0.2054 - 1.25 \cdot y)^{1.25} \cdot (0.7634 - 0.5 \cdot y)^{0.5}) = 2.308, \quad (10)$$

where 2,308 - combined equilibrium constant of reaction (1).

To solve this and subsequent equations program Maple 14 is used.

1st variant of the reaction (1). As described above, in this variant there are no concentration limits and the working equation is equation (10).

The results of solving the 1-st option. The equilibrium mole run of reaction (1) $y(1) = 0.149455 \text{ kmole}$.

The equilibrium mole-equity N and C molar concentrations of species:

- oxygen:

$$N(O_2) = (0.2054 - 1.25 \cdot y) / (1 - 1.75 \cdot y) = 0.0252 (2.52\%), \quad (11)$$

- nitrogen:

$$N(N_2) = (0.7634 - 0.5 \cdot y) / (1 - 1.75 \cdot y) = 0.9326 (93.26\%), \quad (12)$$

– *nitrate-ion*:

$$C(\text{NO}_3^-) = y / v = 0.02015302 \text{ M.} \quad (13)$$

Acidity:

$$C(\text{H}^+) = (y + 0.7781 \cdot 10^{-7}) / v = 0.02015 \text{ M,} \quad (14)$$

$$\text{pH} = -\lg(C(\text{H}^+) \cdot \gamma(\text{H}^+)) = 1.8365. \quad (15)$$

Molar exergies:

– *oxygen*:

$$W(\text{O}_2) = -RT \cdot \ln(N(\text{O}_2)) = 9.1284 \text{ kJ/mole,} \quad (16)$$

– *nitrogen*:

$$W(\text{N}_2) = -RT \cdot \ln(N(\text{N}_2)) = 0.1325 \text{ kJ/mole} \quad (17)$$

As we can see, the implementation of the 1st embodiment reaction nitrogen fixation, ie, without the concentration limits, which is similar to the reaction (1) with the participation of air and distilled water, the oxygen content of the atmosphere in equilibrium should decrease to a value of 2.52 % and nitrogen content should be increased to 93.26%. The oxygen and nitrogen standard exergies meet values $W(\text{O}_2) = 9.1284 \text{ kJ/mole}$ and $W(\text{N}_2) = 0.13248 \text{ kJ/mole}$, i. e, oxygen exergy increased and nitrogen exergy decreased in comparison with the currently accepted values of 3.95 and 0.692 kJ / mole, respectively [1-11].

In such equilibrium state of environment the oceanic water will turn into nitric acid solution with a concentration of 0.02015 kmole/m³ and the pH drops to a value 1.8365.

HNO₃ interaction with calcium and magnesium carbonates [13] (dissolved bicarbonates, crystalline carbonate in the sediments and reefs), resulting in a pH of seawater having reached its current value of 8.12 [11] could hinder the development of such a catastrophic scenario for the earth's biosphere in the past. This mode of ocean can be called "buffer", which corresponds to the above 2nd variant of the reaction (1), which we are going to consider now.

2nd variant of the reaction (1). As described above, in this variant the reaction (1) occurs at pH = 8,12. This case corresponds to the equation (18) obtained by substituting $y = 0$ in the expression (6) $C(\text{H}^+)$ and further equation (10):

$$7.781 \cdot 10^{-8} \cdot y \cdot (1 - 1.75 \cdot y)^{1.75} / ((0.2054 - 1.25 \cdot y)^{1.25} \cdot (0.7634 - 0.5 \cdot y)^{0.5}) = 2.308. \quad (18)$$

The results of solving the 2-nd option. The equilibrium mole run of reaction (1) according to the 2-nd variant of the process: $y(2) = 0.16431986 \text{ kmole}$.

The equilibrium mole-equity N and C molar concentrations of species:

– *oxygen*:

$$N(\text{O}_2) = (0.2054 - 1.25 \cdot y) / (1 - 1.75 \cdot y) = 0.253 \cdot 10^{-6} \quad (2.53 \cdot 10^{-5}\%, 0.253 \text{ ppm}),$$

– *nitrogen*:

$$N(\text{N}_2) = (0.7634 - 0.5 \cdot y) / (1 - 1.75 \cdot y) = 0.9562 \quad (95.62\%),$$

– *nitrate-ion*:

$$C(\text{NO}_3^-) = y / v = 0.02216 \text{ M.}$$

Acidity:

$$C(\text{H}^+) = (y + 0.7781 \cdot 10^{-7}) / v = 1.049 \cdot 10^{-8} \text{ M,}$$

$$\text{pH} = -\lg(C(\text{H}^+) \cdot \gamma(\text{H}^+)) = 8.12.$$

Molar exergies:

– *oxygen*:

$$W(\text{O}_2) = -RT \cdot \ln(N(\text{O}_2)) = 37.66 \text{ kJ/mole,}$$

– *nitrogen*:

$$W(\text{N}_2) = -RT \cdot \ln(N(\text{N}_2)) = 0.111 \text{ kJ/mole.}$$

The characteristics of the 2nd option of equilibrium reaction (1) are analogous to the characteristics of the 1st option, but expressed more clearly. O₂ content in the atmosphere decreases to $2.53 \cdot 10^{-5}\%$, or 0.253 ppm, and the content of N₂ increased to 95.62%. NO₃⁻ ion concentration is increased to 0.02216 M and pH = 8.12, i. e, stored at a predetermined level, indicating the high accuracy of the solution of the equation (18). The following values the standard molar exergies of the air constituents meet the solution: $W(\text{O}_2) = 37.66 \text{ kJ/mole}$, $W(\text{N}_2) = 0.111 \text{ kJ/mole}$.

From the results obtained as the calculation of the equilibrium characteristics of the atmosphere in contact with the ocean we accept the characteristics of the 2nd embodiment, the reaction (1). The 1st option is rejected because the calculation found unrealistically high water acidity (pH = 1.84), which under natural conditions is neutralized by carbonates.

The resulting numerical value is high enough for the molar exergy O₂ suggests that the air also have large mole exergy, nitrogen contributing to the calculation:

O₂:

$$w(\text{O}_2) = 0.2054 \cdot (37.66 + 2.4789 \cdot \ln 0.2054) = 6.9294 \text{ kJ/mole,}$$

N₂:

$$w(\text{N}_2) = 0.7634 \cdot (0.111 + 2.4789 \cdot \ln 0.7634) = -0.5582 \text{ kJ/mole.}$$

Molar exergy of the atmosphere air:

$$W(\text{air}) = 6.9294 - 0.5582 = 6.37 \text{ kJ/mole.}$$

Conclusion. We made calculations of equilibrium of the reaction of nitrogen fixation in the ocean environment in the presence of oxygen under stand-

ard conditions - a temperature of 298.15 K and a pressure of 101.325 kPa pH = 8.12, namely:

1) The equilibrium mole-equity N and C molar concentrations of spices:

– oxygen:

$$N(\text{O}_2) = 0.2527 \cdot 10^{-6} \quad (2.527 \cdot 10^{-5}\%, 0.253 \text{ ppm}),$$

– nitrogen:

$$N(\text{N}_2) = 0.9562 \quad (95.62\%),$$

– nitrate-ion:

$$C(\text{NO}_3^-) = 0.02216 \text{ M};$$

2) exergies of oxygen, nitrogen and air, kJ/mole: $W(\text{O}_2) = 37.66$, $W(\text{N}_2) = 0.111$, $W(\text{air}) = 6.37$.

It is shown that in equilibrium atmosphere the content of O_2 should be very small - 0,253 ppm. This result clearly contrasts with the high and almost stationary (by the standards of human life) oxygen content in the atmosphere (≈ 21 mol. %) And low content of nitrate ion in the ocean water ($3 \cdot 10^{-5}$ M), indicating a highly non-equilibrium state of oxygen in the atmosphere and explains the presence of oxygen and a large exergy in the free state, and in the composition of air. This implies that the air is not a "gratuitous" real stream.

The analysis of the mechanism of maintaining a high content of O_2 in the atmosphere is beyond the scope of this article, but a big role of denitration processes in the ocean and in the soil under the influence of organic reducing agents that are formed by photosynthesis of CO_2 under the influence of irreversible flow of radiant energy of the sun and life fito-flora.

References

1. Szargut, J. Exergy Method. Technical and Ecological Applications / J. Szargut. – Boston: WIT PRESS: Southhampton, 2005.

2. Szargut, J. Chemical Exergies of the Elements / J. Szargut // Applied Chemistry. – 1989. – Vol. 32. – P. 269–286.

3. Szargut, J. International progress in second law analysis / J. Szargut // Energy. – 1980. – Vol. 5. – P. 709–718.

4. Szargut, J. Standard chemical exergy of some elements and their compounds based upon the concentration in the Earth's crust / J. Szargut //

Bull. Polish Acad. Sci., Techn. Ser. – 1987. – Vol. 35. – P. 53–60.

5. Szargut, J. Exergy / J. Szargut, R. Petela. – Warsaw: WNT, 1965.

6. Evaluation of reference exergies for the elements / H. Kameyama [et al.] // Appl. Energy. – 1982. – Vol. 11. – P. 69–82.

7. Szargut, J. L'energie utilisable des substances chimiques inorganiques / J. Szargut, K. Dziedziewicz // Entropie. – 1971. – Vol. 40. – P. 14–23.

8. Szargut, J. Calculation of the standard chemical exergy of some elements and their compounds upon the sea water as a datum level substance / J. Szargut, D. R. Morris // Bull. Pol. Acad. Sci., Techn. Ser. – 1985. – Vol. 33. – P. 293–305.

9. Pinaev, G. F. 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 / G. F. Pinaev // J. of Engineering Phys. and Thermophysics. – 2006. – Vol. 79. – P. 1028–38.

10. Pinaev, G. F. Standard reference exergies of chemical elements in the oceanic reference medium. II. Estimation of the equilibrium of ecospecies in the oceanic medium / G. F. Pinaev // J. of Engineering Phys. and Thermophysics. – 2006. – Vol. 79. – P. 1039–49.

11. Rivero, R. Standard chemical exergy or elements updated / R. Rivero, M. Garfias // Energy. – 2006. – Vol. 31. – P. 3310–26.

12. Sillen, L. G. Regulation of O_2 , N_2 and CO_2 in the atmosphere – thoughts of a laboratory chemist / L. G. Sillen // Tellus. – 1966. – Vol. 18, N 2. – P. 198–206.

13. Ahrendts, J. Reference states / J. Ahrendts // Energy. – 1980. – Vol. 5. – P. 667–77.

14. Encyclopedia of Oceanic Sciences / ed. K. K. Turekian // Acad. Press Elsevier. – 2001. – Vol. 1–6.

15. The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic substances in SI units // Journal of Physical and Chemical Reference Data. – 1982. – Vol. 11, N 2.

16. Turner, D. R. Marine Electrochemistry / D. R. Turner, M. Whitfield. – New York: John Wiley & Sons Ltd, 1981.

Received 22.02.2013

