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Generalized Electron Balance (GEB) as the Law of Nature in Electrolytic Redox Systems

Anna Maria Michałowska-Kaczmarczyk,
Aneta Spórna-Kucab and Tadeusz Michałowski

Additional information is available at the end of the chapter

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Abstract

This chapter refers to fundamental/general/obligatory regularities of electrolytic systems. The linear combination $2 \cdot f(\text{O}) - f(\text{H})$ of elemental balances, $f(\text{H})$ for H and $f(\text{O})$ for O, provides a rigorous criterion distinguishing between redox and non-redox systems is presented as the general relation distinguishing between electrolytic redox and non-redox systems in aqueous media. As the linearly independent equation for a redox system, $2 \cdot f(\text{O}) - f(\text{H})$ is considered as the primary form of the generalized electron balance (GEB), perceived as a law of nature, as the hidden connection of physicochemical laws and the breakthrough in thermodynamic theory of electrolytic redox systems. GEB completes the set of $2+K$ equations necessary for thermodynamic resolution of redox systems according to generalized approach to electrolytic systems (GATES) applying all relevant, physicochemical knowledge available. GATES/GEB, perceived as an example of excellent paradigm, provides the best thermodynamic approach to electrolytic redox systems of any degree of complexity, in aqueous, non-aqueous, and mixed-solvent media. The formulation of GEB does not need prior knowledge of oxidation numbers for all elements in components forming any electrolytic system, within GATES/GEB, the stoichiometry, oxidation number, oxidant, reductant and equivalent mass are as derivative concepts.

Keywords: electrolytic redox systems, approach I to GEB, approach II to GEB, GATES/GEB

1. Introduction

According to the principles assumed in the generalized approach to electrolytic systems (GATES) introduced/formulated by Michałowski in 1992 [1], a balancing of any electrolytic

system is based on the rules of conservation of particular elements/cores Y_g ($g = 1, \dots, G$), and on a charge balance (ChB) expressing the rule of electroneutrality of this system. The closed systems, separated from its environment by diathermal walls, are considered for modelling purposes. The elemental $f(E_g)$ or/and core $f(\text{core}_g)$ balances are denoted briefly as $f(Y_g)$ ($f(E_g)$ or $f(\text{core}_g)$). The balance for the g th element (E_g) or core (core_g) is expressed by the equation interrelating the numbers of g th atom or core in components as units composing the system with the numbers of atoms or cores of g th kind in the species of the system thus formed. For ordering purposes, we assume $E_1 = \text{H}$ (hydrogen) and $E_2 = \text{O}$ (oxygen); then, we have $f(\text{H})$ for $Y_1 = E_1 = \text{H}$, $f(\text{O})$ for $Y_2 = E_2 = \text{O}$, etc. Free water particles and water bound in hydrates are included in balances for $f(\text{H})$ and $f(\text{O})$.

The ChB interrelates the charged species (ions) in this system. A core is a cluster of elements with defined composition, expressed by its chemical formula, structure and external charge, which remains unchanged in a system considered, e.g. SO_4^{-2} in Eq. (54).

The rules of conservation, formulated according to GATES principles [1–36], have the form of algebraic equations related to closed systems, composed of condensed (e.g. liquid, liquid + solid, etc.) phases separated from its environment by diathermal (freely permeable by heat) walls; it enables the heat exchange between the system and its environment. Any chemical process, such as titration, is carried out under isothermal conditions, in a *quasistatic* manner; constant temperature ($T = \text{constant}$) is one of the conditions securing constancy of equilibrium constant values. Any exchange of the matter (H_2O , CO_2 , O_2, \dots) between the system and its environment is thus forbidden for modelling purposes.

We refer first to aqueous media, where the species $X_i^{z_i}$ exist as hydrates $X_i^{z_i} \cdot n_{iW}$; $z_i = 0, \pm 1, \pm 2, \dots$ is a charge, expressed in terms of elementary charge unit, $e = F/N_A$ ($F = 96485.333 \text{ C/mol}$, Faraday's constant; $N_A = 6.022141 \cdot 10^{23} \text{ mol}^{-1}$, Avogadro's number; $n_i (\equiv n_{iW} \equiv n_{i\text{H}_2\text{O}}) \geq 0$ is a mean number of water ($W = \text{H}_2\text{O}$) molecules attached to $X_i^{z_i}$; the case $n_{iW} = 0$ is then also admitted. For ordering purposes, we assume $X_2^{z_2} \cdot n_{2W} = \text{H}^{+1} \cdot n_{2W}$, $X_3^{z_3} \cdot n_{3W} = \text{OH}^{-1} \cdot n_{3W}$, ..., i.e. $z_2 = 1, z_3 = -1, \dots$. Molar concentration of the species $X_i^{z_i} \cdot n_{iW}$ is denoted as $[X_i^{z_i}]$. The $n_i = n_{iW}$ values are virtually unknown, even for $X_2^{z_2} = \text{H}^{+1}$ [37] in aqueous media, and depend on ionic strength (I) of the solution. The $X_i^{z_i}$ s with different numbers of H_2O molecules involved, e.g. H^{+1} , H_3O^{+1} , $\text{H}_9\text{O}_4^{+1}$; $\text{H}_4\text{IO}_6^{-1}$, IO_4^{-1} ; $\text{H}_2\text{BO}_3^{-1}$, $\text{B}(\text{OH})_4^{-1}$; AlO_2^{-1} and $\text{Al}(\text{OH})_4^{-1}$ are considered equivalently [27], i.e. as the same species in this medium. The ChB interrelates charged species (ions, $z_j \neq 0$) in the system.

From $f(\text{H})$ and $f(\text{O})$, the linear combination $2 \cdot f(\text{O}) - f(\text{H})$ is formulated and termed as the primary form of generalized electron balance (GEB), *pr*-GEB = $2 \cdot f(\text{O}) - f(\text{H})$, obtained according to approach II to GEB; this leitmotiv will be extended in further parts of this chapter. The GEB is the immanent part of GATES; the computer software applied to redox systems is denoted as GATES/GEB [1]. When related to redox systems, GATES is based on the generalized electron balance (GEB) [1–36] concept, perceived as a law of nature [1, 2, 14, 15, 22], as the hidden connection of physicochemical laws, as a breakthrough in the theory of electrolytic redox

systems. The GATES refers to mono- and poly-phase, redox and non-redox, equilibrium and metastable [38–42] static and dynamic systems, in aqueous, non-aqueous and mixed-solvent media [26, 29] and in liquid-liquid extraction systems [16, 43].

The generalized electron balance (GEB) concept, discovered by Michałowski as the approach I in 1992 and approach II in 2006 to GEB, plays the key role in redox systems; both approaches are equivalent:

$$\therefore \text{approach II to GEB} \Leftrightarrow \text{approach I to GEB}$$

The GEB is fully compatible with charge balance (ChB) and concentration balances $f(Y_g)$ ($g = 3, \dots, G$), formulated for different elements and cores Y_g . The elemental $f(E_g)$ or/and core $f(\text{core}_g)$ balances are transformed into concentration balances: $\text{CB}(Y_g)$ for $g = 3, \dots, G$.

To avoid redundant terms/naming, the acronyms ChB and GEB are applied both to equations, expressed in terms of particular units (N_i, N_{0j}), or in terms of molar concentrations. On the basis of Eqs. (1a) and (1b) exemplified in Eqs. (2a) and (2b), this should not cause any misinterpretations. Then, $i \in \langle 1, I \rangle$ enumerate species, $j \in \langle 1, J \rangle$ enumerate components, $g \in \langle 0, G \rangle$ enumerate equations for ChB ($g = 0$) and elements/cores: $g = 1$ for H, $g = 2$ for O, $g \in \langle 3, G \rangle$ for other elements/cores, i.e. $Y_1 = \text{H}$, $Y_2 = \text{O}, \dots$, for ordering purposes.

The terms components and species are distinguished. In the notation applied here, N_{0j} ($j = 1, 2, \dots, J$) is the number of molecules of components of j th kind composing the static or dynamic D + T system, whereby the D and T are composed separately, from defined components, including water. The mono- or two-phase electrolytic system thus obtained involve N_1 molecules of H_2O and N_i species of i th kind, $X_i^{z_i} \cdot n_{iW}$ ($i = 2, 3, \dots, I$), specified briefly as $X_i^{z_i}$ (N_i, n_i), where $n_i \equiv n_{iW} \equiv n_i\text{H}_2\text{O}$; then, we have H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3),.... Thus, the components form a (sub)system, and the species $X_i^{z_i} \cdot n_{iW}$ enter the system thus formed. A solid $X_i^{z_i} \cdot n_{iW}$ (precipitate, $z_i = 0$), as a species in a two-phase system, is marked by bold letters, e.g. **I_{2(s)}** and **AgCl**.

In *Example 1* (Section 4.1), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is one of components, and $\text{Cu}(\text{OH})_3^{-1} \cdot n_9\text{H}_2\text{O}$ is one of the species in the system. N_{01} molecules of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ involve $10N_{01}$ atoms of H, $9N_{01}$ atoms of O and N_{01} atoms of Cu, and N_{01} atoms of S. The notation $\text{Cu}(\text{OH})_3^{-1} (N_9, n_9)$ refers to N_9 ions of $\text{Cu}(\text{OH})_3^{-1} \cdot n_9\text{H}_2\text{O}$ involving $N_9(3 + 2n_9)$ atoms of H, $N_9(3 + n_9)$ atoms of O and N_9 atoms of Cu.

Molar concentration $[X_i^{z_i}]$ of $X_i^{z_i} \cdot n_{iW}$ is as follow:

$$\begin{aligned} \text{(a)} \quad [X_i^{z_i}] &= 10^3 \cdot (N_i/N_A)/V_0 \text{ for a static system, or} \\ \text{(b)} \quad [X_i^{z_i}] &= 10^3 \cdot (N_i/N_A)/(V_0 + V) \text{ for a dynamic D + T system} \end{aligned} \tag{1}$$

In a static or dynamic system, the balances are ultimately expressed in terms of molar concentrations of compounds and species, like the expressions for equilibrium constants. In particular, the charge balance (ChB) formulated as follows:

$$\sum_{i=2}^I z_i \cdot N_i = 0 \quad (2)$$

interrelates charged ($z_i \neq 0$) species of this system. In terms of molar concentrations [mol/L] (Eq. (1a) or (1b)), the charge balance has the form

$$\sum_{i=2}^I z_i \cdot [X_i^{z_i}] = 0 \quad (2a)$$

where $z_1 = 0$ for $X_1^{z_1} = \text{H}_2\text{O}$, $z_2 = +1$ for $X_2^{z_2} = \text{H}^+$, $z_3 = -1$ for $X_3^{z_3} = \text{OH}^-$, ...

In non-aqueous and mixed-solvent media, with amphiprotic (co)solvent(s) involved, we assume/allow the formation of mixed solvates $X_i^{z_i} \cdot n_{i1}n_{i2} \dots n_{iS}$, where $n_{is} = n_{iA_s} (\geq 0)$ are the mean numbers of A_s ($s = 1, \dots, S$) molecules attached to $X_i^{z_i}$. We apply the notation $X_i^{z_i}(N_i, n_{iA_1}, n_{iA_2}, \dots, n_{iA_S})$, where N_i is a number of entities of these species in the system [25, 27, 28, 44–46].

2. Preliminary information

The balances $f(Y_g)$ and ChB will be related to some dynamic redox and non-redox systems for comparative purposes. The balances for a given system are combined according to linear combination principles, and some general properties of the resulting balances are indicated.

The components and species in redox systems are involved in GEB, charge (ChB) and elemental balances. All the balances are founded on the well-established physical, physico-chemical and chemical rules involved with charge and all elements conservation, and on the so-named mass action law (MAL), with its ‘old-fashioned’ principles. However, to be fully compatible with the GATES idea, introduced to avoid the stoichiometric reasoning, the equilibrium law (EL), suggested by Michałowski in 2016, was put instead of MAL; the principle of EL formulation is based on the idea of Lagrange multipliers for searching the local extrema of a function that subjects some constraints, expressed by GEB, ChB and concentration balances. The Gibbs free energy G is applied here as a function of the measurable, intensive properties: p and T and the numbers of constituents are convenient in the study of chemical reaction equilibrium. The problem in question is then consistent with the GATES formulation.

The generalized equivalent mass (GEM) concept, suggested by Michałowski in 1979 [11, 19, 47] is also based on the GATES principles, contrary to IUPAC recommendations [48] based on the stoichiometry of chemical reactions. Within GATES, the stoichiometric reaction notations are used only to formulate the expressions for the set of equilibrium constants related to the system in question, not to one ‘representative’ reaction, selected arbitrarily.

Within GATES, the mass conservation law is not limited only to components/species of one, specified/ ‘responsible’ chemical reaction equation but relates to all components/species of an

electrolytic system. The mass change involved with an (exo- or endothermal) effect is negligible when compared with the total mass of the system. For example, the mass change, Δm , involved with enthalpy ΔH° of the reaction $\text{H}_{2(\text{g})} + 0.5\text{O}_{2(\text{g})} = \text{H}_2\text{O}_{(\text{l})}$ ($\Delta H^\circ = -286 \text{ kJ/mol H}_2\text{O}$), equal $\Delta m = \Delta H^\circ/c^2 = -3.18 \cdot 10^{-9} \text{ g}$, is negligible (not measurable) when compared with 18 g of H_2O ; $c = 299,792,458 \text{ m/s}$ is the speed of light in vacuum. The neutralization or dilution gives much smaller heat effects. The resulting law of mass preservation is then fulfilled, irrespectively on whether stoichiometric or non-stoichiometric chemical reactions occur (or do not occur) in the system.

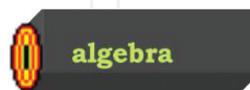
All considerations made in this chapter refer, in principle, to the systems where the elements are formed by stable/non-radioactive isotopes [2], i.e. where no nuclear (α , β^+ , β^- , or electron capture) transformations occur [7], with emission of γ and/or X-ray radiation. However, it is possible to extend the description of redox systems on the systems with radioactive elements, in which the concentrations of the respective components are expressed by dependencies, identified as Bateman's system of linear differential equations [49–52], binding quantitatively the radioactive elements with products of their decay. Radioactive elements and their decay products are also included in the balances for other elements and dependencies for the equilibrium constants.

3. Linear dependence of algebraic equations and transformation into identity

Linear combination of algebraic equations plays a fundamental/decisive role in thermodynamics of electrolytic systems, considered according to GATES [1]. An elementary information related to linear combination, perceived (mainly) from mathematical/algebraic viewpoint, can be found in Ref. [23]. It should be noted that the results of simple addition, i.e. $f_1 + f_2$ and simple subtraction, i.e. $f_1 - f_2$ or $f_2 - f_1$, are also linear combinations of any equations f_1 and f_2 .

We refer here to the problem of linear dependency of balances, analogous to the problem of dependency of linear equations, considered in elementary algebra, see the picture below. In this context, the general property of linear independency, inherently involved with redox systems, will be emphasized.

(1) For the beginning, let us take the set of linear equations:



$$a_{11}x_1 + a_{12}x_2 + a_{13}x_3 = b_1 \quad (3)$$

$$a_{21}x_1 + a_{22}x_2 + a_{23}x_3 = b_2 \quad (4)$$

completed by the linear combination of these equations, i.e.

$$\begin{aligned}
& c_1(a_{11}x_1 + a_{12}x_2 + a_{13}x_3) + c_2(a_{21}x_1 + a_{22}x_2 + a_{23}x_3) \\
& \equiv (c_1a_{11} + c_2a_{21})x_1 + (c_1a_{12} + c_2a_{22})x_2 + (c_1a_{13} + c_2a_{23})x_3 = c_1b_1 + c_2b_2.
\end{aligned} \tag{5}$$

Applying the matrix algebra, we see that the determinant

$$D = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ c_1a_{11} + c_2a_{21} & c_1a_{12} + c_2a_{22} & c_1a_{13} + c_2a_{23} \end{vmatrix} \tag{6}$$

has zero value

$$D = c_1 \cdot \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{11} & a_{12} & a_{13} \end{vmatrix} + c_2 \cdot \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{21} & a_{22} & a_{23} \end{vmatrix} = c_1 \cdot 0 + c_2 \cdot 0 = 0 \tag{7}$$

irrespectively on the c_1 and c_2 values; at $D = 0$, calculation of x_1 , x_2 and x_3 is then impossible.

(2) Let us consider the set of $G + 1$ equations: $f_g(\mathbf{x}) = \varphi_g(\mathbf{x}) - b_g = 0$, where $g = 0, 1, \dots, G$, $\mathbf{x}^T = (x_1, \dots, x_I)$ – transposed (^T) vector \mathbf{x} , composed of independent (scalar) variables x_i ($i \in \langle 1, I \rangle$); a_{gi} , $b_g \in \mathcal{R}$ are independent (explicitly) on \mathbf{x} . After multiplying the equations by the numbers $\omega_g \in \mathcal{R}$ and addition of the resulting equations, we get the linear combination $\sum_{g=0}^G \omega_g \cdot f_g(\mathbf{x}) = 0 \Leftrightarrow \sum_{g=0}^G \omega_g \cdot \varphi_g(\mathbf{x}) = \sum_{g=0}^G \omega_g \cdot b_g$ of the basic equations.

Formation of linear combinations is applicable to check the linear dependency or independence of the balances. A very useful/effective manner for checking/stating the linear dependence of the balances is the transformation of an appropriate system of equations to the identity, $0 = 0$ [2, 23]. For this purpose, we will try, in all instances, to obtain the simplest form of the linear combination. To facilitate these operations, carried out by cancellation of the terms on the left and right sides of equations after changing sides of these equations, we apply the equivalent forms of the starting equations $f_g(\mathbf{x}) = 0$:

$$f_g(\mathbf{x}) : \quad \varphi_g(\mathbf{x}) - b_g = 0 \Leftrightarrow \varphi_g(\mathbf{x}) = b_g \Leftrightarrow -f_g(\mathbf{x}) : \quad -\varphi_g(\mathbf{x}) = -b_g \Leftrightarrow b_g = \varphi_g(\mathbf{x}) \tag{8}$$

In this notation, $f_g(\mathbf{x})$ will be essentially treated not as the algebraic expression on the left side of the equation $f_g(\mathbf{x}) = 0$, but as an equation that can be expressed in alternative forms presented above.

We refer now to the set of linear, algebraic equations

$$\sum_{i=1}^I a_{gi} \cdot x_i = b_g \Leftrightarrow \sum_{i=1}^I a_{gi} \cdot x_i - b_g = 0, \quad (g = 0, 1, \dots, G) \tag{9}$$

where a_{gi} are the coefficients and b_g is the free terms. Multiplying Eq. (9) by ω_g , after subsequent summation and rearrangement, we have

$$\sum_{g=0}^G \omega_g \cdot \sum_{i=1}^I a_{gi} \cdot x_i = \sum_{g=0}^G \omega_g \cdot b_g \Leftrightarrow \sum_{i=1}^I x_i \cdot \sum_{g=0}^G \omega_g \cdot a_{gi} = \sum_{g=0}^G \omega_g \cdot b_g \quad (10)$$

Assuming

$$b_g = \sum_{j=1}^J b_{gj} \cdot x_{0j} \quad (11)$$

from Eqs. (10) and (11) we have

$$\sum_{i=1}^I x_i \cdot \sum_{g=0}^G \omega_g \cdot a_{gi} = \sum_{j=1}^J x_{0j} \cdot \sum_{g=0}^G \omega_g \cdot b_{gj} \quad (12)$$

Referring to the problem in question, and placing $x_i = N_i$, $x_{0j} = N_{0j}$ in Eq. (11), we write

$$b_g = \sum_{j=1}^J b_{gj} \cdot N_{0j} \quad (11a)$$

Then for ChB (Eq. (2a)), where the right side equals zero, we have

$$b_0 = \sum_{j=1}^J b_{0j} \cdot N_{0j} = 0 \quad \text{for } b_{0j} = 0 \quad (j = 1, \dots, J) \quad (13)$$

$$\sum_{i=1}^I N_i \cdot \sum_{g=0}^G \omega_g \cdot a_{gi} = \sum_{j=1}^J N_{0j} \cdot \sum_{g=0}^G \omega_g \cdot b_{gj} \quad (14)$$

The charge balance (ChB) is expressed by Eqs. (2a) and (2b), where $X_i^{z_i}$ is defined by Eq. (1a) (for a static system) or Eq. (1b) (for a dynamic system). The elemental/core balances: $f(H)$, $f(O)$ and $f(Y_g)$ ($Y_g \neq H, O, g = 3, \dots, G$) are written as follows:

$$f_1 = f(H) = \sum_{i=1}^I (a_{1i} + 2n_i) \cdot N_i - \sum_{j=1}^J b_{1j} \cdot N_{0j} = 0 \quad \text{for } Y_1 = H,$$

$$f_2 = f(O) = \sum_{i=1}^I (a_{2i} + n_i) \cdot N_i - \sum_{j=1}^J b_{2j} \cdot N_{0j} = 0 \quad \text{for } Y_2 = O, \dots, \quad (15)$$

$$f_g = \sum_{i=1}^I a_{gi} \cdot N_i - \sum_{j=1}^J b_{gj} \cdot N_{0j} = 0, \dots, f_G = \sum_{i=1}^I a_{Gi} \cdot N_i - \sum_{j=1}^J b_{Gj} \cdot N_{0j} = 0$$

where a_{gi} and b_{gj} are the numbers of atoms/cores of g th kind in the i th species as a constituent of the system and in the component of j th kind, respectively. Denoting, for a moment, $\omega_1 = -1$, $\omega_2 = 2$, we transform the balance

$$f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(\text{O}) - f(\text{H}) = \sum_{i=2}^I (2a_{2i} - a_{1i}) \cdot N_i - \sum_{j=1}^J (2b_{2j} - b_{1j}) \cdot N_{0j} = 0 \Rightarrow \quad (16)$$

$$f_{12} = \omega_1 \cdot \left(\sum_{i=2}^I (a_{1i} \cdot N_i - \sum_{j=1}^J b_{2j} \cdot N_{0j}) \right) + \omega_2 \cdot \left(\sum_{i=2}^I (a_{2i} \cdot N_i - \sum_{j=1}^J (b_{2j} \cdot N_{0j})) \right) \quad (17)$$

$$= \omega_1 \cdot f_1^* + \omega_2 \cdot f_2^* = 0$$

In Eq. (17), f_1^* and f_2^* have the shape similar to the general expression for f_g ($g = 3, \dots, G$) in Eq. (15).

In the balances related to aqueous media, the terms involved with water, i.e. N_{0j} (for j related to H_2O , as the component), N_1 , and all $n_i = n_{iW}$ are not involved (in f_0, f_3, \dots, f_G) or are cancelled within f_{12} (Eq. (17)). Other species, such as CH_3COOH transformable (mentally, purposefully) into $\text{C}_2\text{H}_4\text{O}_2 \equiv \text{C}_2(\text{H}_2\text{O})_2$, and the species in which H and O are not involved in $X_i^{z_i}$ are also cancelled within f_{12} .

On the basis of relations (13) and (17), the linear combination of $G + 1$ balances $f_0, f_{12}, f_3, \dots, f_G$ expressed by Eq. (14) can be presented in equivalent forms:

$$\sum_{i=2}^I N_i \cdot \left(z_i + \sum_{g=1}^G \omega_g \cdot a_{gi} \right) = \sum_{j=1}^J N_{0j} \cdot \sum_{g=1}^G \omega_g \cdot b_{gj} \quad (18)$$

$$\sum_{i=2}^I N_i \cdot z_i + \sum_{g=1}^G \omega_g \cdot \left(\sum_{i=2}^I N_i \cdot a_{gi} - \sum_{j=1}^J N_{0j} \cdot b_{gj} \right) = 0 \quad (18a)$$

$$f_0 + f_{12} + \sum_{g=3}^G \omega_g \cdot f_g = 0$$

$$\text{ChB} + (2 \cdot f(\text{O}) - f(\text{H})) + \sum_{g=3}^G \omega_g \cdot f(Y_g) = 0 \quad (18b)$$

$$(+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + \sum_{g=3}^G (-\omega_g) \cdot f(Y_g) - \text{ChB} = 0$$

All multipliers at N_i and N_{0j} in Eq. (18a) are cancelled simultaneously, if we have

$$z_i + \sum_{g=1}^G \omega_g \cdot a_{gi} = 0 \quad \text{and} \quad \sum_{g=1}^G \omega_g \cdot b_{gj} = 0 \quad (19)$$

for all $i = 1, \dots, I$ and $j = 1, \dots, J$; then Eq. (18) is transformed into identity

$$\sum_{i=1}^I N_i \cdot 0 = \sum_{j=1}^J N_{0j} \cdot 0 \Leftrightarrow 0 = 0 \quad (20)$$

Transformation of a set of the equations into the identity, $0 = 0$, proves the linear dependence between the equations considered. Then from Eq. (18a), we have

$$f_{12} = \sum_{g=3}^G (-\omega_g) \cdot f_g - f_0 \quad (18c)$$

i.e. f_{12} is the dependent balance.

Briefly, from $G + 1$ starting balances: $f_0, f_1, f_2, f_3, \dots, f_G$ we obtain G balances: $f_0, f_{12}, f_3, \dots, f_G$. If f_{12} is the dependent balance, we have $G - 1$ independent balances: f_0, f_3, \dots, f_G ; it is the case related to non-redox systems. If f_{12} is the independent balance, we have G independent balances: $f_0, f_{12}, f_3, \dots, f_G$, that will be rearranged, optionally, as the set $(f_{12}, f_0, f_3, \dots, f_G)$ related to GEB, ChB and $f(Y_g)$ ($g = 3, \dots, G$), respectively. The number of elemental/core balances $f(Y_g)$ ($Y_g \neq \text{H}, \text{O}, g = 3, \dots, G$) and then the number of concentration balances CB(Y_g) in redox systems equals $K = G - 2$.

As stated above, the linear combination of $2 \cdot f(\text{O}) - f(\text{H})$ with ChB and elemental/core balances $f(Y_g)$ ($g = 3, \dots, G$) provides the criterion distinguishing between non-redox and redox systems of different complexity [3, 23]. To obtain the simplest form of the linear combination, some useful/general rules allowing to select multipliers ω_g of the corresponding balances are suggested. Namely, the ω_g values in Eq. (10) are equal to the oxidation numbers of the electron-non-active elements in the related system. The proper linear combination of the balances is reducible (a) to the identity, $0 = 0$, for non-redox systems or (b) to the simplest equation different from (not reducible to) the identity, but involving some terms related to the species and components of the system. This way we state that $2 \cdot f(\text{O}) - f(\text{H})$ is linearly dependent on the other balances in non-redox systems, i.e. it is not a new/independent balance in such systems. In redox systems, the balance $2 \cdot f(\text{O}) - f(\text{H})$ and its linear combinations with ChB and $f(Y_g)$ ($g = 3, \dots, G$) are the new equation, completing, as the generalized electron balance (GEB), the set of equations needed for resolution of electrolytic redox systems.

Static and dynamic non-redox and redox systems, with water as the main component, are considered. A static system of volume V_0 mL is obtained by disposable mixing different components. The dynamic system is realized according to the titrimetric mode. At defined point of the titration $\text{B} (C, V) \Rightarrow \text{A} (C_0, V_0)$, denoted briefly as $\text{T} \Rightarrow \text{D}, V$ mL of titrant T containing the component B (C mol/L) is added into V_0 mL of titrand D containing the component A (C_0 mol/L), and $V_0 + V$ mL of D + T system/mixture is thus obtained, if the assumption of volume additivity is valid/tolerable; then D and T are sub-systems of the D + T system. The progress of the titration is represented by the fraction titrated Φ [11, 19, 47, 53, 54] value

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \quad (21)$$

For comparative purposes, we first refer to non-redox systems, where the derivation of relevant formulas will be carried out in detail also for training purposes. The regularities resulting from these examples, namely linear dependency of (linear) algebraic equations stated for non-redox electrolytic systems, will provide the reference point for further parts of this chapter, where redox systems are considered. Further examples in this chapter, related only to redox systems, will be presented in a synthetic manner, indicating the similarities and differences in the respective equations. The conclusions drawn here will provide the basis for further, important generalizations.

4. Linear combination of balances for non-redox systems

4.1. Examples

Example 1 (static): V_0 mL of CuSO_4 solution is prepared from N_{01} molecules of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and N_{02} molecules of H_2O . The resulting solution consists of the following species: H_2O (N_1), H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3), HSO_4^{-1} (N_4, n_4), SO_4^{-2} (N_5, n_5), Cu^{+2} (N_6, n_6), CuOH^{+1} (N_7, n_7), $\text{Cu}(\text{OH})_2$ (N_8, n_8), $\text{Cu}(\text{OH})_3^{-1}$ (N_9, n_9), $\text{Cu}(\text{OH})_4^{-2}$ (N_{10}, n_{10}) and CuSO_4 (N_{11}, n_{11}). The components and species are involved in the balances for particular elements, Y_g : H, O, Cu, S, i.e.

$$f_1 = f(\text{H}) :$$

$$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + N_4(1 + 2n_4) + N_5 2n_5 + N_6 2n_6 + N_7(1 + 2n_7) + N_8(2 + 2n_8) + N_9(3 + 2n_9) + N_{10}(4 + 2n_{10}) + N_{11} 2n_{11} = 10N_{01} + 2N_{02} \quad (22)$$

$$f_2 = f(\text{O}) :$$

$$N_1 + N_2 n_2 + N_3(1 + n_3) + N_4(4 + n_4) + N_5(4 + n_5) + N_6 n_6 + N_7(1 + n_7) + N_8(2 + n_8) + N_9(3 + n_9) + N_{10}(4 + n_{10}) + N_{11}(4 + n_{11}) = 9N_{01} + N_{02} \quad (23)$$

$$f_{12} = 2 \cdot f(\text{O}) - f(\text{H}) : -N_2 + N_3 + 7N_4 + 8N_5 + N_7 + 2N_8 + 3N_9 + 4N_{10} + 8N_{11} = 8N_{01} \quad (24)$$

$$f_0 = \text{ChB} : N_2 - N_3 - N_4 - 2N_5 + 2N_6 + N_7 - N_9 - 2N_{10} = 0 \quad (25)$$

$$-2f_3 = -2f(\text{Cu}) : 2N_{01} = 2N_6 + 2N_7 + 2N_8 + 2N_9 + 2N_{10} + 2N_{11} \quad (26)$$

$$-6f_4 = -6f(\text{S}) = -6f(\text{SO}_4) : 6N_{01} = 6N_4 + 6N_5 + 6N_{11} \quad (27)$$

Simple addition of the elemental/core balances (Eqs. (24)–(27)) gives the identity

$$2 \cdot f(\text{O}) - f(\text{H}) + \text{ChB} - 2f(\text{Cu}) - 6f(\text{S}) = 0 \Rightarrow (+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+2) \cdot f(\text{Cu}) + (+6) \cdot f(\text{S}) - \text{ChB} = 0 \Rightarrow 0 = 0 \quad (28)$$

As we see, the multipliers ω_g in the transformed identity are equal to oxidation numbers of the indicated elements.

Example 2 (dynamic): V_0 mL of CuSO_4 solution, as a titrand D composed of N_{01} molecules of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and N_{02} molecules of H_2O , is titrated with V mL of titrant T, composed of N_{03} molecules of NaOH and N_{04} molecules of H_2O , added up to a defined point of the titration. In the resulting D + T mixture (two-phase system of volume ca. $V_0 + V$ mL), we have the species as in Example 1 and, additionally: $\text{Cu}(\text{OH})_2$ (N_{12} , n_{12}), Na^+ (N_{13} , n_{13}). From the balances:

$$f_1 = f(\text{H}) : (\dots) + N_{12}(2 + 2n_{12}) + 2N_{13}n_{13} = (\dots) + N_{03} + 2N_{04} \quad (29)$$

$$f_2 = f(\text{O}) : (\dots) + N_{12}(2 + n_{12}) + N_{13}n_{13} = (\dots) + N_{03} + N_{04} \quad (30)$$

$$f_{12} = 2 \cdot f(\text{O}) - f(\text{H}) : -N_2 + N_3 + 7N_4 + 8N_5 + N_7 + 2N_8 + 3N_9 + 4N_{10} + 8N_{11} + 2N_{12} = 8N_{01} + N_{03} \quad (31)$$

$$f_0 = \text{ChB} : N_2 - N_3 - N_4 - 2N_5 + 2N_6 + N_7 - N_9 - 2N_{10} + N_{13} = 0 \quad (32)$$

$$-2f_3 = -2f(\text{Cu}) : 2N_{01} = 2N_6 + 2N_7 + 2N_8 + 2N_9 + 2N_{10} + 2N_{11} + 2N_{12} \quad (33)$$

$$-6f_4 = -6f(\text{S}) = -6f(\text{SO}_4) : 6N_{01} = 6N_4 + 6N_5 + 6N_{11} \quad (34)$$

$$-f_5 = -f(\text{Na}) : N_{03} = N_{13} \quad (35)$$

That means we obtain the identity, $0 = 0$, for

$$2 \cdot f(\text{O}) - f(\text{H}) + \text{ChB} - f(\text{Na}) - 2 \cdot f(\text{Cu}) - 6 \cdot f(\text{S}) = 0 \Rightarrow \\ (+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+2) \cdot f(\text{Cu}) + (+6) \cdot f(\text{S}) - \text{ChB} = 0 \quad (36)$$

The terms within (...)’s in Eqs. (29) and (30) are the same as in Eqs. (22) and (23).

4.2. A comment

The equations for $f(\text{H})$ and $f(\text{O})$ involve the numbers $n_i = n_{iW}$ of hydrating water molecules, attached to particular species. In the linear combinations $2 \cdot f(\text{O}) - f(\text{H})$, all the n_{iW} are cancelled, together with N_1 , i.e. the n_{iW} and N_1 do not enter the equation for $2 \cdot f(\text{O}) - f(\text{H})$. The n_{iW} is not involved in ChB and in $f(Y_j)$ for $Y_j \neq \text{H}, \text{O}$ and then they are not introduced in the linear combinations of $2 \cdot f(\text{O}) - f(\text{H})$ with these equations. The multipliers ω_g in Eq. (10) are equal to oxidation numbers of particular elements involved in the related elemental/core balances. Then, the linear combination of the balances related to a non-redox system, when put in context with Eqs. (19) and (20) gives the identity $0 = 0$. This regularity is obligatory for all non-redox systems considered above (*Examples 1 and 2*), and elsewhere, e.g. [22, 37, 55]. Note that $2 \cdot f(\text{O}) - f(\text{H})$ involves $-N_2 + N_3$, whereas ChB involves $N_2 - N_3 = -(-N_2 + N_3)$, and the related terms are cancelled within the combination $2 \cdot f(\text{O}) - f(\text{H}) + \text{ChB}$. Moreover, all components related to the species $X_i^{z_i} \cdot n_{iW}$, not involving H and/or O in $X_i^{z_i}$, are cancelled too within $2 \cdot f(\text{O}) - f(\text{H})$.

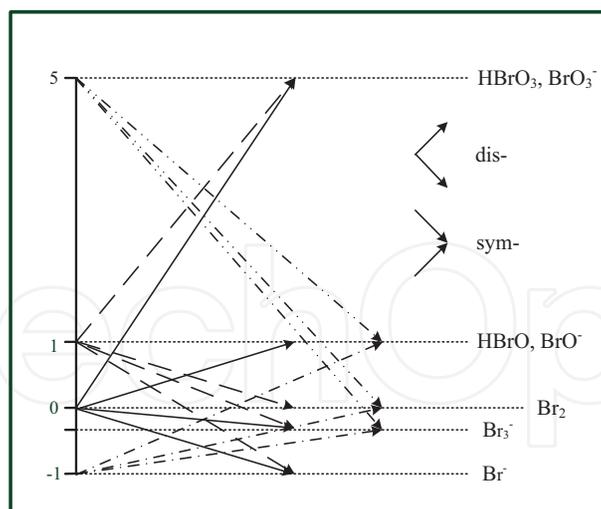


Figure 1. Schemes of disproportionation and symproportionation within bromine species [5].

In further sections, we formulate the balances for redox systems containing one, two or three electron-active elements in redox systems (aqueous media), where the complete set of expressions for independent equilibrium constants interrelating concentrations of different species is involved. We start our considerations from the systems with one electron-active element involved with disproportionation and symproportionation [5, 13, 15, 16, 19]. These properties are appropriate for the elements that form compounds and species at three or more oxidation degrees. In particular, bromine (Br) forms the species on five oxidation degrees ($-1, -1/3, 0, 1, 5$), see **Figure 1**, e.g. 0 (for Br_2) and 1 (for HBrO or NaBrO) $\in (-1, 5)$. There are possible transitions between different bromine species, associated with changes of the oxidation states of this element, see **Figure 1**.

5. Disproportionating systems

5.1. Formulation of balances for $\text{NaOH} (C, V) \Rightarrow \text{Br}_2 (C_0, V_0)$ system

5.1.1. Approach II to GEB

Note that V_0 mL of the titrand D composed of $\text{Br}_2 (N_{01}) + \text{H}_2\text{O} (N_{02})$ is titrated with V mL of titrant T composed of $\text{NaOH} (N_{03}) + \text{H}_2\text{O} (N_{04})$. For the $V_0 + V$ mL of the D + T mixture, with the set of the species completed by $\text{Na}^+ (N_{11}, n_{11})$.

The balances can be formulated as follows:

$$\begin{aligned}
 f_1 = f(\text{H}) : \\
 2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + N_4(1 + 2n_4) + 2N_5n_5 + N_6(1 + 2n_6) + 2N_7n_7 + 8N_8n_8 \\
 + 2N_9n_9 + 2N_{10}n_{10} + N_{11}(1 + 2n_{11}) = 2N_{02} + N_{03} + 2N_{04}
 \end{aligned}
 \tag{37}$$

$$f_2 = f(\text{O}) :$$

$$N_1 + N_2n_2 + N_3(1 + n_3) + N_4(3 + n_4) + N_5(3 + n_5) + N_6(1 + n_6) + N_7(1 + n_7) + N_8n_8 \quad (38)$$

$$+ N_9n_9 + N_{10}n_{10} + N_{11}(1 + n_{11}) = N_{02} + N_{03} + N_{04}$$

$$f_0 = \text{ChB} : \quad N_2 - N_3 - N_5 - N_7 - N_9 - N_{10} + N_{11} = 0 \quad (39)$$

$$-f_3 = -f(\text{Na}) : \quad N_{03} = N_{11} \quad (40)$$

$$f_4 = f(\text{Br}) : \quad N_4 + N_5 + N_6 + N_7 + 2N_8 + 3N_9 + N_{10} - 2N_{01} = 0 \quad (41)$$

Then we formulate the linear combinations:

$$f_{12} = 2 \cdot f(\text{O}) - f(\text{H}) : \quad -N_2 + N_3 + 5N_4 + 6N_5 + N_6 + 2N_7 = N_{03} \quad (42)$$

$$f_{012} = f_{12} + f_0 : \quad 5(N_4 + N_5) + N_6 + N_7 - N_9 - N_{10} + N_{11} = 0 \quad (43)$$

$$f_{0123} = f_{12} + f_0 - f_3 : \quad 5(N_4 + N_5) + N_6 + N_7 - N_9 - N_{10} = 0 \quad (44)$$

$$f_{01234} = (f_{0123} + f_4)/2 : \quad 3(N_4 + N_5) + N_6 + N_7 + N_8 + N_9 = N_{01} \quad (45)$$

For comparative purposes, we formulate also the linear combination $Z_{\text{Br}}f_3 - f_{0123}$

$$(Z_{\text{Br}} - 5)(N_4 + N_5) + (Z_{\text{Br}} - 5)(N_6 + N_7) + 2Z_{\text{Br}}N_8 + (3Z_{\text{Br}} + 1)N_9 + (Z_{\text{Br}} + 1)N_{10} = 2Z_{\text{Br}}N_{01} \quad (46)$$

where $Z_{\text{Br}} = 35$ is the atomic number for bromine (Br).

All the linear combinations (42)–(46) are not reducible to identity, $0 = 0$; in the simplest case, we have six constituents (species, components) involved in f_{0123} (Eq. (44)). Eqs. (42)–(46) are equivalent forms of GEB, expressed in terms of particular constituents (components, species). To express them in terms of molar concentrations, we apply the relations: (1a) and $C_0 \cdot V_0 = 10^3 \cdot N_{01}/N_A$, $CV = 10^3 \cdot N_{03}/N_A$. In this way, we consider the titration of V_0 mL of Br_2 (C_0 mol/L) solution with V mL of C mol/L NaOH solution added up to a defined point of the titration. In particular, from Eq. (46), we have the balance for GEB

$$(Z_{\text{Br}} - 5)([\text{HBrO}_3] + [\text{BrO}_3^{-1}]) + (Z_{\text{Br}} - 1)([\text{HBrO}] + [\text{BrO}^{-1}]) + 2Z_{\text{Br}}[\text{Br}_2] \\ + (3Z_{\text{Br}} + 1)[\text{Br}_3^{-1}] + (Z_{\text{Br}} + 1)[\text{Br}^{-1}] = 2Z_{\text{Br}}C_0V_0/(V_0 + V) \quad (46a)$$

completed by the balances for ChB, CB(Br) and CB(Na):

$$[\text{H}^{+1}] - [\text{OH}^{-1}] + [\text{Na}^{+1}] - [\text{BrO}_3^{-1}] - [\text{BrO}^{-1}] - [\text{Br}_3^{-1}] - [\text{Br}^{-1}] = 0 \quad (46b)$$

$$[\text{HBrO}_3] + [\text{BrO}_3^{-1}] + [\text{HBrO}] + [\text{BrO}^{-1}] + 2[\text{Br}_2] + 3[\text{Br}_3^{-1}] + [\text{Br}^{-1}] - 2C_0V_0/(V_0 + V) = 0 \quad (46c)$$

$$[\text{Na}^{+1}] = CV/(V_0 + V) \quad (46d)$$

5.1.2. Approach I to GEB

The (optional) formulas for GEB, expressed by Eqs. (42)–(46), were obtained according to approach II to GEB, based on $pr\text{-GEB} = 2 \cdot f(\text{O}) - f(\text{H})$. In this section, we apply the approach I to GEB, known also as the ‘short’ version of GEB, where prior knowledge of oxidation numbers of all elements in the system is assumed/required.

In the $\text{NaOH} (C, V) \Rightarrow \text{Br}_2 (C_0, V_0)$ system considered in Section 4.2, bromine is the only electron-active element, considered as the carrier of its own, bromine electrons. One atom of Br has Z_{Br} bromine electrons, and then one molecule of Br_2 has $2Z_{\text{Br}}$ bromine electrons, i.e. N_{01} molecules of Br_2 involve $2Z_{\text{Br}} \cdot N_{01}$ bromine electrons. The oxidation degree x of an atom in simple species, such as ones formed here by bromine, is calculated on the basis of known oxidation degrees: +1 for H and –2 for O and external charge of this species. Then for HBrO_3 , we have, by turns: $1 \cdot 1 + 1 \cdot x + 3 \cdot (-2) = 0 \Rightarrow x = 5$; for BrO_3^{-1} : $1 \cdot x + 3 \cdot (-2) = -1 \Rightarrow x = 5$; for HBrO : $1 \cdot 1 + 1 \cdot x + 1 \cdot (-2) = 0 \Rightarrow x = 1$, etc.

The oxidation number is the net charge resulting from the presence of charge carriers, inherently involved in an atom: protons in nuclei and orbital electrons, expressed in elementary charge units – as +1 for protons and –1 for electrons. The number y of bromine electrons in one molecule of HBrO_3 is calculated from the formula: $Z_{\text{Br}} \cdot (+1) + y \cdot (-1) = 5$, i.e., bromine in HBrO_3 involves $y = Z_{\text{Br}} - 5$ bromine electrons, etc. On this basis, we state that [15]

N_4 species $\text{HBrO}_3 \cdot n_4 \text{H}_2\text{O}$ involve	$(Z_{\text{Br}} - 5) \cdot N_4$	bromine electrons;
N_5 species $\text{BrO}_3^{-1} \cdot n_5 \text{H}_2\text{O}$ involve	$(Z_{\text{Br}} - 5) \cdot N_5$	bromine electrons;
N_6 species $\text{HBrO} \cdot n_6 \text{H}_2\text{O}$ involve	$(Z_{\text{Br}} - 1) \cdot N_6$	bromine electrons;
N_7 species $\text{BrO}^{-1} \cdot n_7 \text{H}_2\text{O}$ involve	$(Z_{\text{Br}} - 1) \cdot N_7$	bromine electrons;
N_8 species $\text{Br}_2 \cdot n_8 \text{H}_2\text{O}$ involve	$2Z_{\text{Br}} \cdot N_8$	bromine electrons;
N_9 species $\text{Br}_3^{-1} \cdot n_9 \text{H}_2\text{O}$ involve	$(3Z_{\text{Br}} + 1) \cdot N_9$	bromine electrons;
N_{10} species $\text{Br}^{-1} \cdot n_{10} \text{H}_2\text{O}$ involve	$(Z_{\text{Br}} + 1) \cdot N_{10}$	bromine electrons;
N_{01} molecules of Br_2 involved	$2Z_{\text{Br}} \cdot N_{01}$	bromine electrons.

Balancing the bromine electrons, we get Eq. (46), and then Eq. (46a), considered as the GEB obtained immediately from the approach I to GEB; this proves the equivalency of approaches I and II to GEB.

5.1.3. Preparation of an algorithm and computer program

Let us refer again to balances (46a)–(46d) interrelating concentrations $[X_i^{z_i}]$ of the species $X_i^{z_i}$ with the total concentrations C_0, C of indicated components of the system. In this place, one should distinguish between the terms equation and equality. The term equation is related here

No.	Reaction	Equilibrium equation	Equilibrium data
1	$\text{BrO}_3^{-1} + 6\text{H}^{+1} + 6\text{e}^{-1} = \text{Br}^{-1} + 3\text{H}_2\text{O}$	$[\text{Br}^{-1}] = K_{e1} \cdot [\text{BrO}_3^{-1}] [\text{H}^{+1}]^6 [\text{e}^{-1}]^6$	$E_{04} = 1.45 \text{ V}$
2	$\text{BrO}^{-1} + \text{H}_2\text{O} + 2\text{e}^{-1} = \text{Br}^{-1} + 2\text{OH}^{-1}$	$[\text{Br}^{-1}] = K_{e2} \cdot [\text{BrO}^{-1}] [\text{H}^{+1}]^2 [\text{e}^{-1}]^2 / K_W^2$	$E_{03} = 0.76 \text{ V}$
3	$\text{Br}_2 + 2\text{e}^{-1} = 2\text{Br}^{-1}$	$[\text{Br}^{-1}]^2 = K_{e3} \cdot [\text{Br}_2] [\text{e}^{-1}]^2$	$E_{03} = 1.087 \text{ V}$
4	$\text{Br}_3^{-1} + 2\text{e}^{-1} = 3\text{Br}^{-1}$	$[[\text{Br}^{-1}]^3 = K_{e4} \cdot [\text{Br}_3^{-1}] [\text{e}^{-1}]^2$	$E_{04} = 1.05 \text{ V}$
5	$\text{HBrO}_3 = \text{H}^{+1} + \text{BrO}_3^{-1}$	$[\text{H}^{+1}] [\text{BrO}_3^{-1}] = K_{51} \cdot [\text{HBrO}_3]$	$\text{p}K_{51} = 0.7$
6	$\text{HBrO} = \text{H}^{+1} + \text{BrO}^{-1}$	$[\text{H}^{+1}] [\text{BrO}^{-1}] = K_{11} \cdot [\text{HBrO}]$	$\text{p}K_{11} = 8.6$
7	$\text{H}_2\text{O} = \text{H}^{+1} + \text{OH}^{-1}$	$[\text{H}^{+1}] [\text{OH}^{-1}] = K_W$	$\text{p}K_W = 14.0$

where $\log K_{e1} = 6A E_{01}$, $\log K_{ei} = 2A E_{0i}$ ($i = 2, 3, 4$); $A = 16.92$; $\text{p}K_{51} = -\log K_{51}$, $\text{p}K_{11} = -\log K_{11}$, $\text{p}K_W = -\log K_W$.

Table 1. Equilibrium data related to different bromine species.

to the balance where at least two species are involved; these species are interrelated by expressions for the corresponding equilibrium constants values (**Table 1**). Such a requirement is fulfilled by Eqs. (46a)–(46c), whereas in Eq. (46d) we have concentration of one species; at any V value, $[\text{Na}^{+1}]$ is a number (not variable) and, as such, it enters immediately ChB (Eq. (46b)).

From the interrelations obtained on the basis of equilibrium data [56] collected in **Table 1** we have

$$\begin{aligned}
 [\text{H}^{+1}] &= 10^{-\text{pH}}; \quad [\text{OH}^{-1}] = 10^{\text{pH}-14}; \quad [\text{BrO}_3^{-1}] = 10^{6A(E-1.45)-\text{pBr}+6\text{pH}}, \\
 [\text{BrO}^{-1}] &= 10^{2A(E-0.76)-\text{pBr}+2\text{pH}-28}; \quad [\text{Br}_2] = 10^{2A(E-1.087)-2\text{pBr}}; \quad [\text{Br}_3^{-1}] = 10^{2A(E-1.05)-2\text{pBr}}, \quad (47) \\
 [\text{HBrO}_3] &= 10^{0.7-\text{pH}} [\text{BrO}_3^{-1}]; \quad [\text{HBrO}] = 10^{8.6-\text{pH}} \cdot [\text{BrO}^{-1}]
 \end{aligned}$$

where the uniformly defined (scalar) variables: E , pH and pBr , forming a vector $\mathbf{x} = (E, \text{pH}, \text{pBr})^T$, are involved; $A \cdot E = -\log[\text{e}^{-1}]$, $\text{pH} = -\log[\text{H}^{+1}]$, $\text{pBr} = -\log[\text{Br}^{-1}]$. All the variables are in the exponents of the power for 10 in $[\text{e}^{-1}] = 10^{-A E}$, $[\text{H}^{+1}] = 10^{-\text{pH}}$, $[\text{Br}^{-1}] = 10^{-\text{pBr}}$. The number of the (independent) variables equals to the number of equations, $K = 2 + 1 = 3$; this ensures a unique solution of the equations, at a pre-set C_0 , C and V_0 values, and the V -value at which the calculations are realized, at a defined step of the calculation procedure, according to iterative computer program presented below.

Computer program for the NaOH_Br2 system

function F = NaOH_Br2(x)

global V C0 V0 C yy

$$E = x(1);$$

$$\text{pH} = x(2);$$

$$\text{pBr} = x(3);$$

$$H = 10^{(-\text{pH})};$$

$$K_W = 10^{-14};$$

$$pK_w = 14;$$

$$OH = K_w/H;$$

$$A = 16.92;$$

$$Br = 10^{-pBr};$$

$$ZBr = 35;$$

$$Br_2 = Br^2 \cdot 10^{(2 \cdot A \cdot (E - 1.087))};$$

$$Br_3 = Br^3 \cdot 10^{(2 \cdot A \cdot (E - 1.05))};$$

$$BrO = Br \cdot 10^{(2 \cdot A \cdot (E - 0.76) + 2 \cdot pH - 2 \cdot pK_w)};$$

$$BrO_3 = Br \cdot 10^{(6 \cdot A \cdot (E - 1.45) + 6 \cdot pH)};$$

$$HBrO = 10^{8.6 \cdot H} \cdot BrO;$$

$$HBrO_3 = 10^{0.7 \cdot H} \cdot BrO_3;$$

$$Na = C \cdot V / (V_0 + V);$$

$$F = [\% \text{Charge balance}$$

$$(H - OH + Na - Br - Br_3 - BrO - BrO_3);$$

$$\% \text{Concentration balance for Br}$$

$$(Br + 3 \cdot Br_3 + 2 \cdot Br_2 + HBrO + BrO + HBrO_3 + BrO_3 - 2 \cdot C_0 \cdot V_0 / (V_0 + V));$$

$$\% \text{Electron balance}$$

$$((ZBr + 1) \cdot Br + (3 \cdot ZBr + 1) \cdot Br_3 + 2 \cdot ZBr \cdot Br_2 + (ZBr - 1) \cdot (HBrO + BrO) \dots$$

$$+ (ZBr - 5) \cdot (HBrO_3 + BrO_3) - 2 \cdot ZBr \cdot C_0 \cdot V_0 / (V_0 + V)];$$

$$yy(1) = \log_{10}(Br);$$

$$yy(2) = \log_{10}(Br_3);$$

$$yy(3) = \log_{10}(Br_2);$$

$$yy(4) = \log_{10}(HBrO);$$

$$yy(5) = \log_{10}(BrO);$$

$$yy(6) = \log_{10}(HBrO_3);$$

$$yy(7) = \log_{10}(BrO_3);$$

$$yy(8) = \log_{10}(Na);$$

end

5.1.4. Preparation of the computer program for NaOH (C, V) ⇒ HBrO (C₀, V₀) system

Modification of the computer program makes it possible to carry out calculations for other systems associated with bromine, e.g. for the system NaOH (C, V) ⇒ HBrO (C₀, V₀). In this case, the changes are made in the following lines:

Computer program for the NaOH_HBrO system

Function F = NaOH_HBrO(x)

```

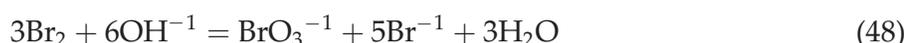
—
      (Br+3*Br3+2*Br2+HBrO+BrO+HBrO3+BrO3-C0*V0/(V0+V));
—
      +(ZBr-5)*(HBrO3+BrO3)-(ZBr-1)*C0*V0/(V0+V));
—

```

5.1.5. Graphical presentation of the data and discussion

The systems considered here are characterized by distinctly marked jumps in *E* and pH values (**Figures 2A** and **B**) at the vicinity of the equivalence points, occurring at $\Phi_{\text{eq1}} = 1$ for NaOH (C, V) → HBrO (C₀, V₀) (system I), and at $\Phi_{\text{eq2}} = 2$ for NaOH (C, V) → Br₂ (C₀, V₀) (system II), see **Table 2** [15, 16].

Reactions occurred in the systems I and II can be formulated from the analysis of the respective speciation diagrams. As results from **Figure 2C**, the disproportionation reaction in the system I occurs according to the scheme



i.e. $\Phi_{\text{eq}} = 2 \Rightarrow CV_{\text{eq1}} = 2C_0V_0$. After crossing the equivalent point, the main products of this disproportionation reaction are Br⁻¹ and BrO₃⁻¹, not Br⁻¹ and BrO⁻¹ corresponding to the reaction



with the same stoichiometry, 3 : 6 = 1 : 2. From detailed calculations at $\Phi = 2.5$, i.e. at an excess of NaOH added, we find $[\text{BrO}_3^{-1}]/[\text{Br}^{-1}] = 10^{-2.574}/10^{-6.7584} = 1.53 \cdot 10^4$, i.e. efficiency of the reaction (48) is more than 4 orders of magnitude greater than the efficiency of reaction (49).

Scheme of Br₂ disproportionation affected by NaOH (C) can also be calculated [16]. At $\Phi = 2.5$, we have $[\text{BrO}_3^{-1}]/[\text{Br}^{-1}] = 10^{-2.574}/10^{-1.875} = 10^{-0.699} = 0.2 = 1:5$, i.e. at an excess of NaOH added (see **Figure 2c**), the disproportionation occurs mainly according to the scheme indicated by reaction (48) from the products side.

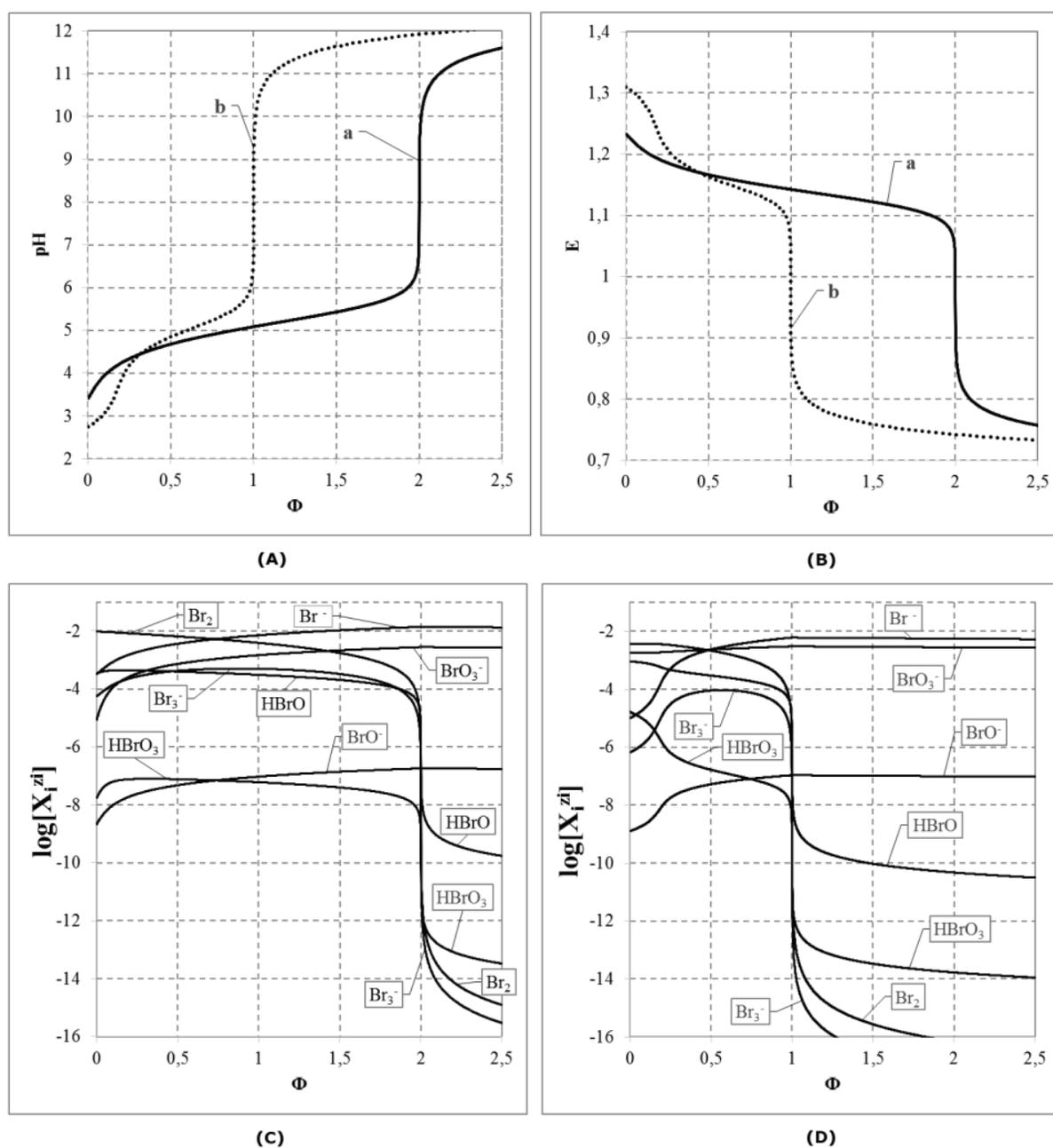


Figure 2. (A) $\text{pH} = \text{pH}(\Phi)$ and (B) $E = E(\Phi)$ relationships plotted for the systems I and II, and the related speciation diagrams for the systems: I (C) and II (D).

In the system II, disproportionation of HBrO affected by NaOH (C) added according to the titrimetric mode is presented in **Figure 2D** [16]. The $[\text{Br}^-]/[\text{BrO}_3^-]$ ratio equals: $10^{-2.2553}/10^{-2.5563}$ at $\Phi = 2.0$; $10^{-2.2730}/10^{-2.5740}$ at $\Phi = 2.5$, i.e. $10^{0.3010} = 2 = 2:1$, corresponding to the stoichiometric ratio of products of this reaction. As results from **Figure 2C**, the disproportionation, at an excess of NaOH added, occurs mainly according to reaction $3\text{HBrO} + 3\text{OH}^- = 2\text{Br}^- + \text{BrO}_3^- + 3\text{H}_2\text{O}$ (stoichiometry 3:3 = 1:1), resulting from half reactions: $\text{HBrO} + 2e^- + \text{H}^+ = \text{Br}^- + \text{H}_2\text{O}$, $\text{HBrO} - 4e^- + 2\text{H}_2\text{O} = \text{BrO}_3^- + 5\text{H}^+$, and $3\text{H}^+ + 3\text{OH}^- = 3\text{H}_2\text{O}$. The

System II			System I		
NaOH (C, V) → HBrO (C ₀ , V ₀)			NaOH (C, V) → Br ₂ (C ₀ , V ₀)		
Φ	pH	E	Φ	pH	E
0.995	6.347	1.0720	1.995	6.666	1.0491
0.996	6.411	1.0681	1.996	6.728	1.0455
0.997	6.498	1.0630	1.997	6.811	1.0406
0.998	6.625	1.0555	1.998	6.933	1.0334
0.999	6.866	1.0412	1.999	7.161	1.0199
1.000	8.102	0.9682	2.000	8.143	0.9619
1.001	9.002	0.9150	2.001	8.966	0.9132
1.002	9.281	0.8985	2.002	9.244	0.8968
1.003	9.450	0.8885	2.003	9.413	0.8868
1.004	9.571	0.8814	2.004	9.534	0.8797
1.005	9.666	0.8758	2.005	9.628	0.8741

Table 2. The sets of rounded (Φ , pH, E) values taken from the vicinity of the equivalence points; $V_0 = 100$, $C_0 = 0.01$, $C = 0.1$.

(Φ , pH, E) values from the close vicinity of the corresponding equivalence points on the curves in **Figures 2A** and **B** are collected in **Table 2**. The Br₂ solution is acidic, as results, e.g. from the ChB (Eq. (29a)): at $[\text{Na}^+] = 0$ ($\Phi = 0$) we have $[\text{H}^+] - [\text{OH}^-] = [\text{BrO}_3^-] + [\text{BrO}^-] + [\text{Br}_3^-] + [\text{Br}^-] > 0$, i.e. $[\text{H}^+] > [\text{OH}^-]$; this inequality is also obtained from Eq. (42), at $N_{03} = 0$: $[\text{H}^+] - [\text{OH}^-] = 5[\text{HBrO}_3] + 6[\text{BrO}_3^-] + [\text{HBrO}] + 2[\text{BrO}^-] > 0$. Br₂ is an acid with a strength comparable to that of acetic acid; at $C_0 = 0.01$, pH equals 3.40 for Br₂ and 3.325 for CH₃COOH ($\text{p}K_1 = 4.65$). Disproportionation of Br₂ occurs initially to a small extent (several %), according to the scheme $\text{Br}_2 + \text{OH}^- = \text{HBrO} + \text{Br}^-$, compare with [57].

In $C_0 = 0.01$ mol/L HBrO solution, more than 90% HBrO disproportionates occur according to the reaction $5\text{HBrO} = \text{BrO}_3^- + 2\text{Br}_2 + 2\text{H}_2\text{O} + \text{H}^+$; at $V = 0$, we have $[\text{Br}_2] = 10^{-2.4406}$, $[\text{BrO}_3^-] = 10^{-2.7442}$, i.e. $[\text{Br}_2]/[\text{BrO}_3^-] = 10^{0.3036} \approx 2$, which confirms this stoichiometry of the reaction. The H^+ ions formed in this reaction acidify the solution significantly: at $C_0 = 0.01$ and $V = 0$, we have pH = 2.74, although HBrO itself is a relatively weak acid.

The numerical values of the concentrations given here are taken from the corresponding files with results of iterative calculations.

5.2. Titration in NaOH (C, V) ⇒ HIO (C₀, V₀) system

The curves plotted in **Figure 3a–c** are related to titration of $V_0 = 10$ mL of HIO ($C_0 = 0.1$ mol/L) with V mL of $C = 0.1$ mol/L NaOH. At the initial part of the titration, we have the reactions:

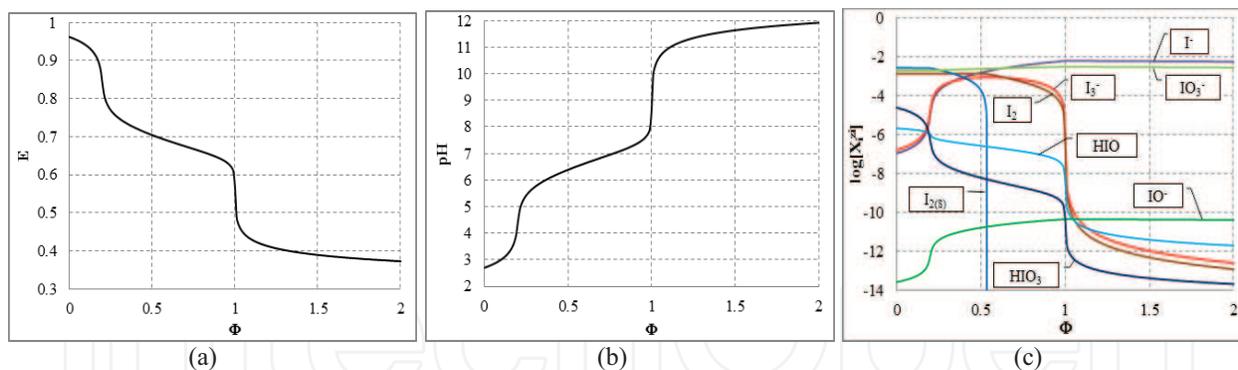
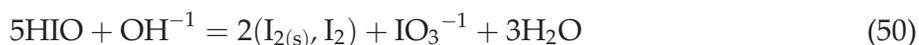
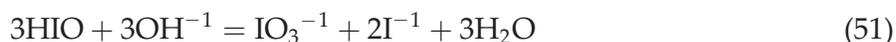


Figure 3. Plots of (a) $E = E(\Phi)$, (b) $\text{pH} = \text{pH}(\Phi)$, and (c) speciation curves for $\text{NaOH} (C, V) \Rightarrow \text{HIO} (C_0, V_0)$ system at $V_0 = 10$, $C_0 = 0.01$, $C = 0.1$.



In the following, at Φ ca. 0.20–0.22, a pronounced increase in $[\text{I}^{-1}]$ occurs, as a result of reaction



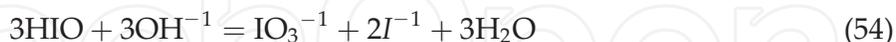
The increase in $[\text{I}^{-1}]$ is accompanied by an increase in $[\text{I}_3^{-1}]$



This leads to the gradual disappearance of $\text{I}_{2(s)}$ (which is ultimately ended at $\Phi = 0.5347$) and lowering of $[\text{I}_2]$ and $[\text{I}_3^{-1}]$; all them disproportionate



At $[\text{I}_{2(s)}] > 0$, we have $[\text{I}_2] = s = \text{const}$; $s = 1.33 \cdot 10^{-3}$ mol/L is the solubility of $\text{I}_{2(s)}$ in water, at 20°C . Finally, the disproportionation of HIO, affected by NaOH, can be expressed by the equation



Note that the stoichiometry of the reaction (54) is $3 : 3 = 1 : 1$, which corresponds to the jump on the curves presented in **Figures 3a,b**, occurring at $\Phi = 1$. For $\Phi > 1$, we have $[\text{I}^{-1}]/[\text{IO}_3^{-1}] = 2$, i.e. the stoichiometry of the products of reaction (54) equals to $1 : 2$. The jumps on the curves $E = E(\Phi)$ and $\text{pH} = \text{pH}(\Phi)$ (**Figures 3a,b**) occur at Φ ca. 0.2 (which corresponds to the stoichiometry 1:5 of the reaction (50)) and at Φ ca. 1 (which corresponds to the stoichiometry 3:3 = 1:1 of the reaction (54)); the maxima on the corresponding derivative curves in **Figures 4a,b** fit the stoichiometric ratios.

5.3. Titration in $\text{HCl} (C, V) \Rightarrow \text{NaIO} (C_0, V_0)$ system

$V_0 = 10$ mL of $C_0 = 0.01$ mol/L NaIO is titrated with $C = 0.1$ mol/L HCl. The related curves are presented in **Figures 5a-d**. Initially, the reaction

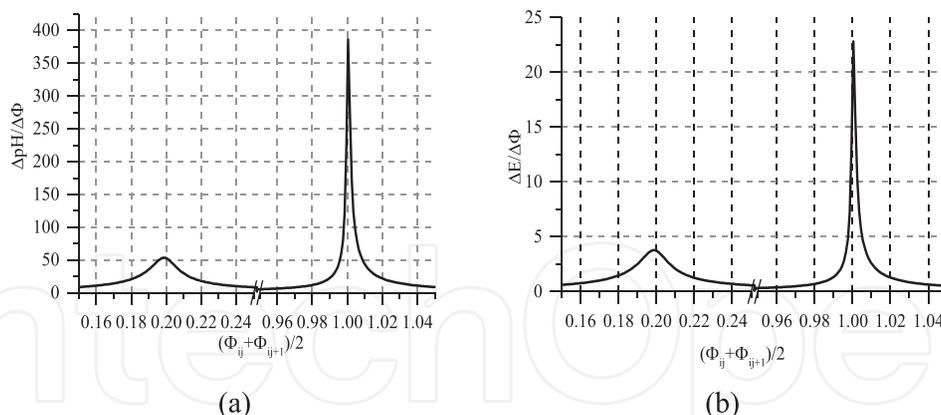


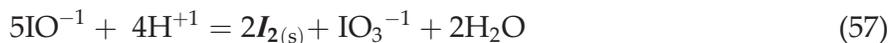
Figure 4. The (a) $\Delta p\text{H}/\Delta\Phi = (p\text{H}_{j+1} - p\text{H}_j)/(\Phi_{j+1} - \Phi_j)$, (b) $\Delta E/\Delta\Phi = (E_{j+1} - E_j)/(\Phi_{j+1} - \Phi_j)$ vs. $\Phi = (\Phi_j + \Phi_{j+1})/2$ relationships for the $\text{NaOH} (C, V) \Rightarrow \text{HIO} (C_0, V_0)$ system.



and then, the reaction



occurs. Then I^{-1} from Eq. (55) and I_2 from Eq. (56) form I_3^{-1} in the reaction $\text{I}_2 + \text{I}^{-1} = \text{I}_3^{-1}$ and $[\text{I}_3^{-1}]$ increases. At $\Phi = 0.4654$, $\text{I}_{2(s)}$ appears as the solid phase

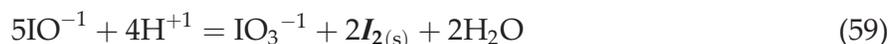


At $[\text{I}_{2(s)}] > 0$, we have $[\text{I}_2] = \text{const}$. The increase in $[\text{Cl}^{-1}]$, resulted from addition of HCl, causes an increase in $[\text{I}_2\text{Cl}^{-1}]$, and—to a lesser extent—the increase in $[\text{ICl}_2^{-1}]$ and $[\text{ICl}]$. The addition of HCl lowers pH of the solution, and then $[\text{HIO}]$ becomes larger than $[\text{IO}^{-1}]$; $[\text{HIO}_3]$ also increases. In effect, the summary concentration $[\text{HIO}] + [\text{IO}^{-1}]$ after addition of an excess of HCl is higher than in the starting NaIO solution.

In the algorithm, we have allowed the participation of Cl^{-1} ions from HCl solution in the redox reaction. However, the concentration of Cl_2 and HClO as the main products of Cl^{-1} oxidation (**Figure 5b**) is quite negligible. This way, one can state that the Cl^{-1} ions practically do not participate in the redox reaction as a reducing agent. From linear combination of reactions (55) and



(multiplication by 5 and 2 respectively), cancellations and division by 3, we get the reaction



with stoichiometry $4:5 = 0.8$, which corresponds to $\Phi = 4:5 = 0.8$, where the inflection point on the curves in **Figures 5c** and **d** are observed. The I^{-1} and I_3^{-1} ions are consumed in reactions (58) and

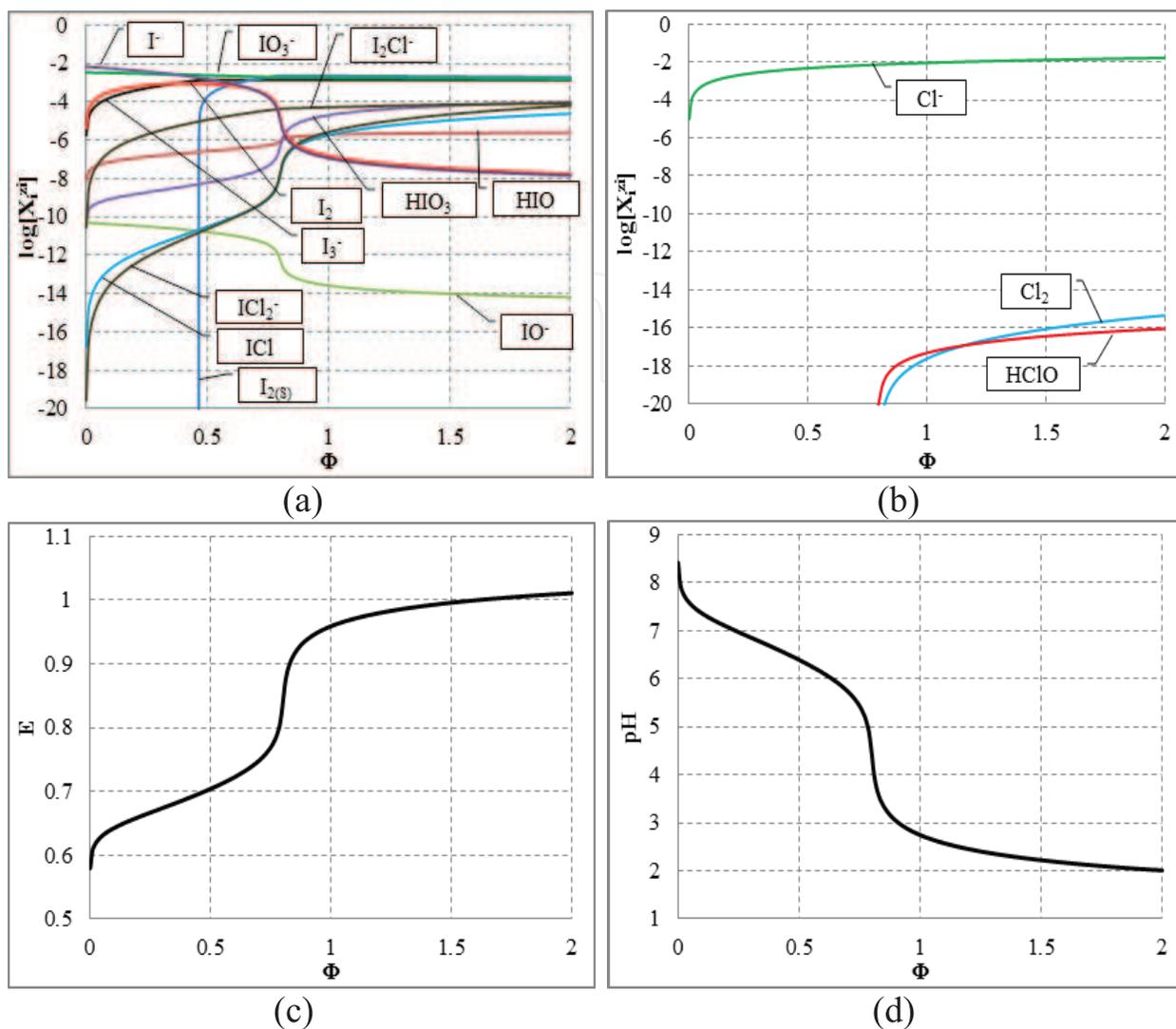


Figure 5. The speciation curves for indicated (a) iodine and (b) chlorine species $X_i^{z_i}$ and (c) $E = E(\Phi)$, (d) $pH = pH(\Phi)$ functions for $HCl(C, V) \Rightarrow NaIO(C_0, V_0)$ system; $V_0 = 10$, $C_0 = 0.01$, $C = 0.1$.



See **Figure 5a**.

Computer program for $HCl(C, V) \Rightarrow NaIO(C_0, V_0)$ system

function F = System_NaIO_HCl(x);

%NaIO<-HCl

% Titration of V_0 mL of NaIO (C_0) with V mL HCl (C).

global V Vmin Vstep Vmax V0 C C0 fi H OH pH E Kw pKw A aa

global I I3 I2 I2s HIO IO HI5O3 I5O3 H5I7O6 H4I7O6 H3I7O6 Na

global logI logI3 logI2 logI2s logHIO logIO logHI5O3 logI5O3 logH5I7O6

global logH4I7O6 logH3I7O6 logNa

global Cl Cl2 HClO ClO HClO2 Cl3O2 Cl4O2 Cl5O3 Cl7O4 I2Cl ICl ICl2

global logCl logCl2 logHClO logClO logHClO2 logCl3O2 logCl4O2 logCl5O3

global logCl7O4 logI2Cl logICl logICl2 pI pCl

$E=x(1);$

$pH=x(2);$

$pI=x(3);$

$pCl=x(4);$

$H=10.^{-pH};$

$pKw=14;$

$Kw=10.^{-14};$

$OH=Kw./H;$

$I=10.^{-pI};$

$Cl=10.^{-pCl};$

$A=16.92;$

$ZCl=17;$

$ZI=53;$

$I2=I.^2.*10.^{(2.*A.*(E-0.621))};$

$I3=I.^3.*10.^{(2.*A.*(E-0.545))};$

$IO=I.*10.^{(2.*A.*(E-0.49)+2.*pH-2.*pKw)};$

$HIO=IO.*10.^{(10.6-pH)};$

$I5O3=I.*10.^{(6.*A.*(E-1.08)+6.*pH)};$

$HI5O3=I5O3.*10.^{(0.79-pH)};$

$H5I7O6=I.*10.^{(8.*A.*(E-1.24)+7.*pH)};$

$H4I7O6=H5I7O6.*10.^{(-3.3+pH)};$

$H3I7O6=I.*10.^{(8.*A.*(E-0.37)+9.*pH-9.*pKw)};$

$Cl2=Cl.^2.*10.^{(2.*A.*(E-1.359))};$

$ClO=Cl.*10.^{(2.*A.*(E-0.88)+2.*pH-2.*pKw)};$

$HClO=ClO.*10.^{(7.3-pH)};$

$$\text{Cl}_3\text{O}_2 = \text{Cl} \cdot 10^{(4 \cdot A \cdot (E - 0.77) + 4 \cdot \text{pH} - 4 \cdot \text{pKw})};$$

$$\text{HCl}_3\text{O}_2 = \text{Cl} \cdot 10^{(4 \cdot A \cdot (E - 1.56) + 3 \cdot \text{pH})};$$

$$\text{Cl}_4\text{O}_2 = \text{Cl} \cdot 10^{(5 \cdot A \cdot (E - 1.5) + 4 \cdot \text{pH})};$$

$$\text{Cl}_5\text{O}_3 = \text{Cl} \cdot 10^{(6 \cdot A \cdot (E - 1.45) + 6 \cdot \text{pH})};$$

$$\text{Cl}_7\text{O}_4 = \text{Cl} \cdot 10^{(8 \cdot A \cdot (E - 1.38) + 8 \cdot \text{pH})};$$

$$\text{I}_2\text{Cl} = \text{I}_2 \cdot 10^{(0.2 - \text{pCl})};$$

$$\text{ICl} = \text{I}_2^{0.5} \cdot 10^{(A \cdot (E - 1.105) - \text{pCl})};$$

$$\text{ICl}_2 = \text{ICl} \cdot 10^{(2.2 - \text{pCl})};$$

$$\text{Na} = \text{C}_0 \cdot \text{V}_0 / (\text{V}_0 + \text{V});$$

if $\text{I}_2 > 1.33\text{e-}3$

$$\text{I}_{2s} = \text{I}_2 - 1.33\text{e-}3;$$

$$\text{I}_2 = 1.33\text{e-}3;$$

$$\text{aa} = 1;$$

else

$$\text{aa} = 0;$$

$$\text{I}_{2s} = 0;$$

end;

%Charge balance

$$\text{F} = [(\text{H-OH} + \text{Na} - \text{I} - \text{I}_3 - \text{IO} - \text{I}_5\text{O}_3 - \text{H}_4\text{I}_7\text{O}_6 - 2 \cdot \text{H}_3\text{I}_7\text{O}_6 - \text{Cl} - \text{ClO} - \text{Cl}_3\text{O}_2 - \text{Cl}_5\text{O}_3 - \text{Cl}_7\text{O}_4 \dots$$

$$- \text{I}_2\text{Cl} - \text{ICl}_2);$$

%Concentration balance for I

$$(\text{I} + 3 \cdot \text{I}_3 + 2 \cdot (\text{I}_2 + \text{aa} \cdot \text{I}_{2s}) + \text{HIO} + \text{IO} + \text{HI}_5\text{O}_3 + \text{I}_5\text{O}_3 + \text{H}_5\text{I}_7\text{O}_6 + \text{H}_4\text{I}_7\text{O}_6 + \text{H}_3\text{I}_7\text{O}_6 + \dots$$

$$2 \cdot \text{I}_2\text{Cl} + \text{ICl} + \text{ICl}_2 - \text{C}_0 \cdot \text{V}_0 / (\text{V}_0 + \text{V}));$$

%Concentration balance for Cl

$$(\text{Cl} + 2 \cdot \text{Cl}_2 + \text{HClO} + \text{ClO} + \text{HCl}_3\text{O}_2 + \text{Cl}_3\text{O}_2 + \text{Cl}_4\text{O}_2 + \text{Cl}_5\text{O}_3 + \text{Cl}_7\text{O}_4 + \text{I}_2\text{Cl} + \text{ICl} \dots$$

$$+ 2 \cdot \text{ICl}_2 - \text{C} \cdot \text{V} / (\text{V}_0 + \text{V}));$$

%Electron balance

$$((\text{ZI} + 1) \cdot \text{I} + (3 \cdot \text{ZI} + 1) \cdot \text{I}_3 + 2 \cdot \text{ZI} \cdot (\text{I}_2 + \text{aa} \cdot \text{I}_{2s}) + (\text{ZI} - 1) \cdot (\text{HIO} + \text{IO}) \dots$$

$$+ (\text{ZI} - 5) \cdot (\text{HI}_5\text{O}_3 + \text{I}_5\text{O}_3) + (\text{ZI} - 7) \cdot (\text{H}_5\text{I}_7\text{O}_6 + \text{H}_4\text{I}_7\text{O}_6 + \text{H}_3\text{I}_7\text{O}_6) + (\text{ZCl} + 1) \cdot \text{Cl} + \dots$$

$2 \cdot ZCl \cdot Cl_2 + (ZCl-1) \cdot (HClO + ClO) + (ZCl-3) \cdot (HCl_3O_2 + Cl_3O_2) \dots$
 $+ (ZCl-4) \cdot Cl_4O_2 + (ZCl-5) \cdot Cl_5O_3 + (ZCl-7) \cdot Cl_7O_4 + (2 \cdot ZI + ZCl+1) \cdot I_2Cl + \dots$
 $(ZI + ZCl) \cdot ICl + (ZI+2 \cdot ZCl+1) \cdot ICl_2 \dots$
 $- ((ZI-1) \cdot C_0 \cdot V_0 + (ZCl+1) \cdot C \cdot V) / (V_0 + V)];$

$\log I = \log_{10}(I);$

$\log I_3 = \log_{10}(I_3);$

$\log I_2 = \log_{10}(I_2);$

$\log I_{2s} = \log_{10}(I_{2s});$

$\log HIO = \log_{10}(HIO);$

$\log IO = \log_{10}(IO);$

$\log HI_5O_3 = \log_{10}(HI_5O_3);$

$\log I_5O_3 = \log_{10}(I_5O_3);$

$\log H_5I_7O_6 = \log_{10}(H_5I_7O_6);$

$\log H_4I_7O_6 = \log_{10}(H_4I_7O_6);$

$\log H_3I_7O_6 = \log_{10}(H_3I_7O_6);$

$\log Cl = \log_{10}(Cl);$

$\log Cl_2 = \log_{10}(Cl_2);$

$\log HClO = \log_{10}(HClO);$

$\log ClO = \log_{10}(ClO);$

$\log HCl_3O_2 = \log_{10}(HCl_3O_2);$

$\log Cl_3O_2 = \log_{10}(Cl_3O_2);$

$\log Cl_4O_2 = \log_{10}(Cl_4O_2);$

$\log Cl_5O_3 = \log_{10}(Cl_5O_3);$

$\log Cl_7O_4 = \log_{10}(Cl_7O_4);$

$\log I_2Cl = \log_{10}(I_2Cl);$

$\log ICl = \log_{10}(ICl);$

$\log ICl_2 = \log_{10}(ICl_2);$

$\log Na = \log_{10}(Na);$

% The end of program

A remark: Some notations applied in this program are as follows: $[\text{HIO}_3] \rightarrow \text{HI5O3}$, $[\text{H}_3\text{IO}_6^{-2}] \rightarrow \text{H3I7O6}$, $[\text{ClO}_2^{-1}] \rightarrow \text{Cl3O2}$, $[\text{ClO}_2] \rightarrow \text{Cl4O2}$, etc.

5.4. Disproportionation in static redox systems

In disproportionating redox systems, it is advisable to check an effect of dilution of the corresponding solutes on values of the corresponding variables. It is advisable to plot the desired relationships in the figures with the values $pC = -\log C$ on the abscissa, where C is the concentration [mol/L] of the solute considered. Formally, the related plots correspond to presentation, in extended logarithmic scale, the results of titration of the initial solution of this solute with pure water as a titrant T.

The static systems with C mol/L solutions of (1) HIO and (2) NaIO are shown graphically in **Figures 6a-c** and **7a-c**, where pH, E and $\log [X_i^{z_i}]$ values related to different concentrations C of the corresponding solutes with the values $pC = -\log C$ on the abscissa.

5.4.1. C mol/L HIO

As results from the speciation diagram in **Figure 6c**, in more concentrated HIO solutions, i.e. at lower pC values, the predominating reactions are as follows: $5\text{HIO} = 2(\text{I}_{2(s)}, \text{I}_2) + \text{IO}_3^{-1} + 2\text{H}_2\text{O} + \text{H}^{+1}$ and $5\text{HIO} = 2(\text{I}_{2(s)}, \text{I}_2) + \text{HIO}_3 + 2\text{H}_2\text{O}$; solubility of $\text{I}_{2(s)}$ $s = 1.33 \cdot 10^{-3}$ mol/L (25°C). At further dilution of HIO, the reaction $3\text{HIO} = 2\text{I}^{-1} + \text{IO}_3^{-1} + 3\text{H}^{+1}$ occurs in an increasing degree. This change in disproportionation scheme, more significant at pC 4–5, resulted in a change of the shapes of the plots: $E = E(pC)$ (**Figure 6a**) and $\text{pH} = \text{pH}(pC)$ (**Figure 6b**).

5.4.2. C mol/L NaIO

The disproportionation of IO^{-1} introduced by NaIO proceeds mainly according to the scheme $3\text{HIO} = \text{IO}_3^{-1} + 2\text{I}^{-1} + 3\text{H}^{+1}$ (see **Figure 7c**), where $[\text{I}^{-1}]/[\text{IO}_3^{-1}] \cong 2$. Concentration of I_2 is lower than 10^{-6} mol/L and then solid $\text{I}_{2(s)}$ is not formed.

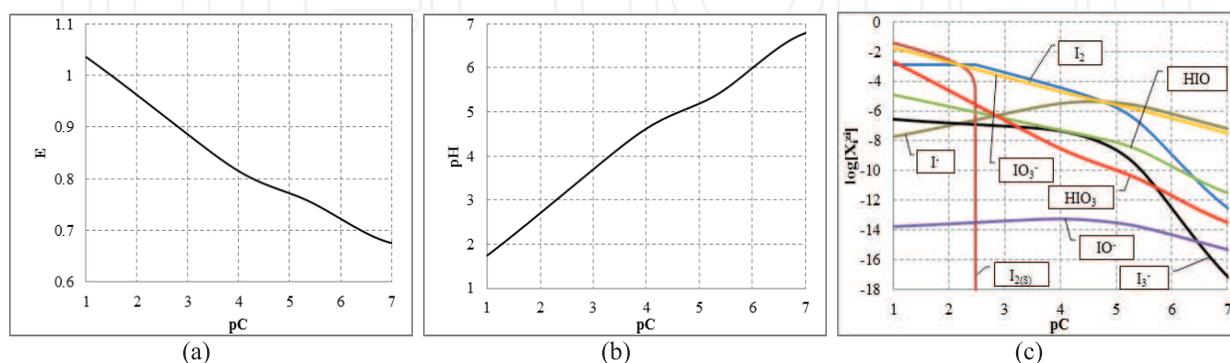


Figure 6. The plots of (a) E vs. pC , (b) pH vs. pC relationships and (c) speciation curves for indicated iodine species $X_i^{z_i}$ in C mol/L HIO.

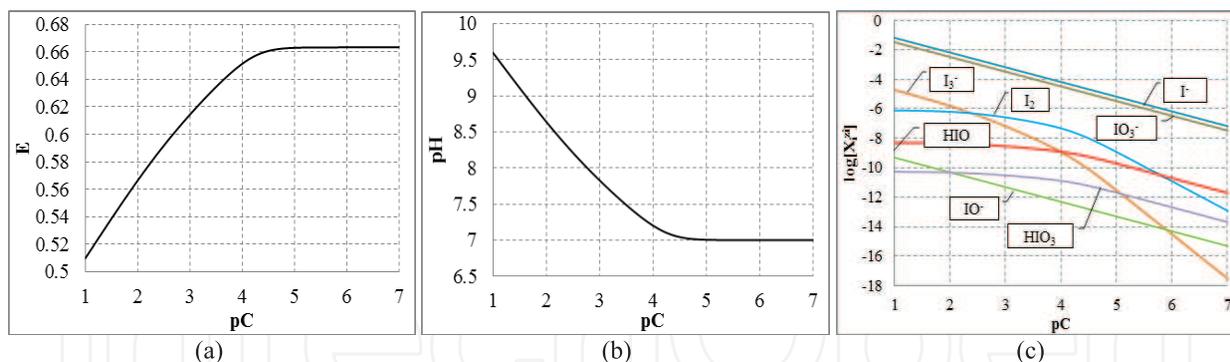


Figure 7. The functions: (a) $E = E(pC)$, (b) $pH = pH(pC)$ and (c) speciation curves for indicated iodine species $X_i^{z_i}$ plotted for C mol/L NaIO.

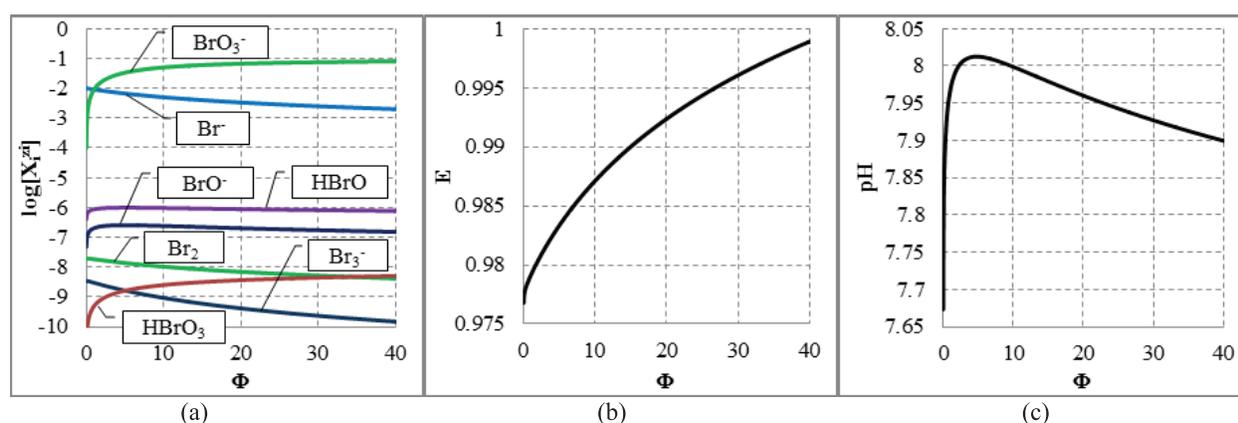


Figure 8. Plots for the $KBrO_3 (C, V) \Rightarrow NaBr (C_0, V_0)$ system: (a) speciation diagram, (b) $E = E(\Phi)$, and (c) $pH = pH(\Phi)$ curves; $V_0 = 10$, $C_0 = 0.01$, $C = 0.1$.

6. Symproportionating systems

6.1. Titration in $KBrO_3 (C, V) \Rightarrow NaBr (C_0, V_0)$ system

In this case, symproportionation practically does not occur (**Figure 8a**); concentration of HBrO, as the major product formed in the symproportionation reaction



is ca. 10^{-6} mol/L. The potential E increases monotonically (**Figure 8b**), whereas pH first increases, passes through maximum and then decreases (**Figure 8c**). The relevant pH and E changes are small. Binding the H^{+1} ions in reaction (61) causes a weakly alkaline reaction (**Figure 8b**).

6.2. Titration in $KBrO_3 (C, V) \Rightarrow NaBr (C_0) + H_2SO_4 (C_{03}) V_0$ system

The stoichiometry 1:5, i.e. $\Phi_{eq} = 0.2$, stated for C_{03} values indicated at the curves plotted in **Figure 9** (column a), results from reaction

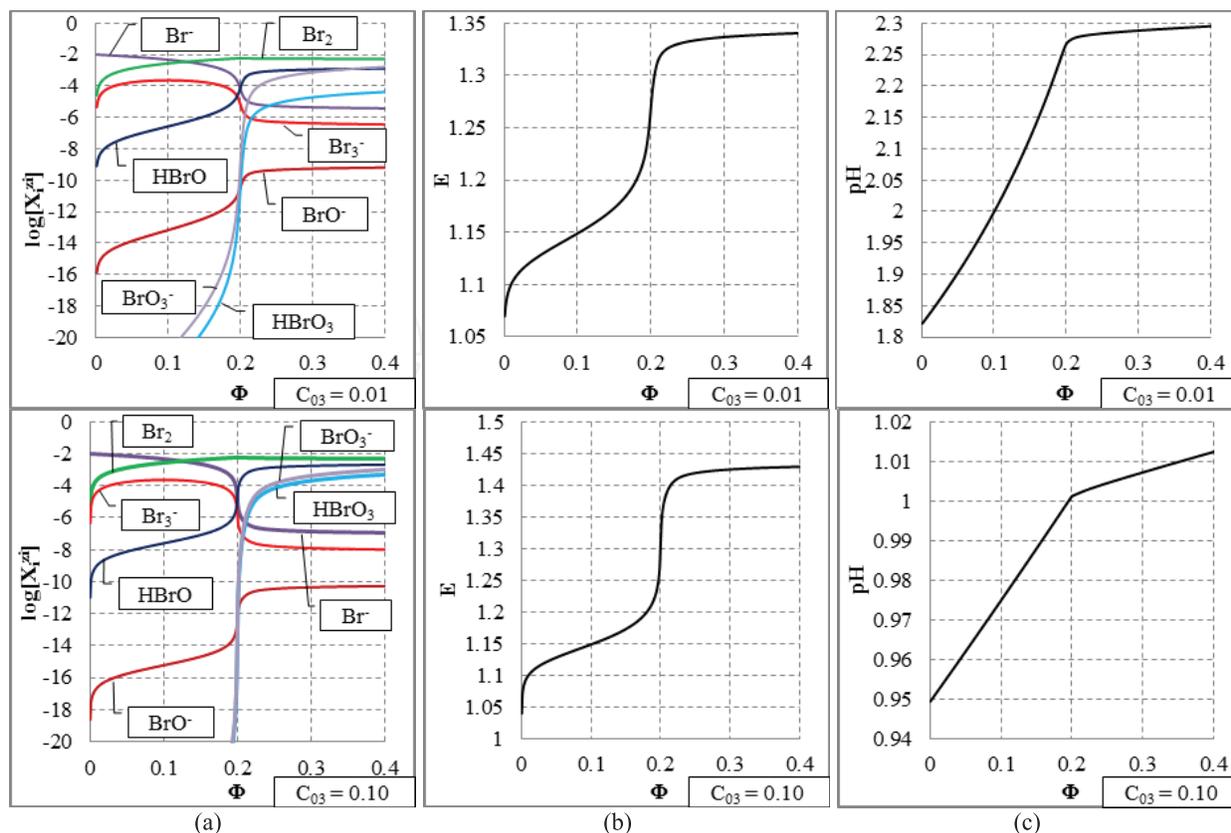
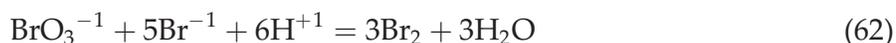


Figure 9. Plots for the $\text{KBrO}_3 (C, V) \Rightarrow \text{NaBr} (C_0) + \text{H}_2\text{SO}_4 (C_{03}) V_0$ system: speciation diagrams (column a); $E = E(\Phi)$ (column b) and $\text{pH} = \text{pH}(\Phi)$ (column c), at $V_0 = 100$, $C_0 = 0.01$, $C = 0.1$ and indicated C_{03} [mol/L] values for H_2SO_4 .



For $\Phi > 0.2$, an increase of efficiency of the competitive reaction



is noted. A growth of C_{03} value causes a small extension of the potential range in the jump region, on the side of higher E values (**Figure 9**, column b). With an increase in the C_{03} value, the graphs of pH vs. Φ resemble two almost straight-line segments intersecting at $\Phi_{\text{eq}} = 0.2$ (**Figure 9**, column c). However, the pH ranges covered by the titration curves are gradually narrowed (**Figure 9**, column c).

7. Redox systems with two electron-active elements

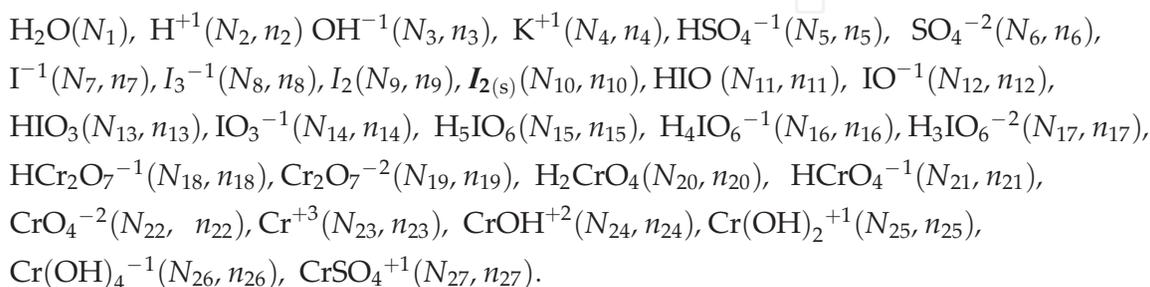
In the redox systems considered above, one electron-active element was involved in disproportionation or symproportionation reactions affected by NaOH (in dynamic systems) or water (in static systems). In the $\text{HCl} (C, V) \Rightarrow \text{NaIO} (C_0, V_0)$ system, where HCl was used as disproportionating reagent, the possibility of oxidation of Cl^{-1} ions was allowed *a priori*, in which HCl was used as a disproportionating reagent, i.e. chlorine in HCl was treated as an

electron-active element. It turned out, however, that the oxidation of Cl^{-1} occurred only in an extremely small extent, ca. $10^{-16}/10^{-2} \approx 10^{-14}$ part of Cl^{-1} ions was oxidized. So, we can consider that it is virtually the disproportionation of IO^{-1} ions originating from the NaIO .

In this section, we consider the systems where two electron-active elements are factually present.

7.1. Titration in $\text{K}_2\text{Cr}_2\text{O}_7$ (C, V) \Rightarrow KI (C₀) + H_2SO_4 (C₀₁) V₀ system

Note that V_0 mL of titrand D composed of KI (N_{03}) + H_2SO_4 (N_{04}) + H_2O (N_{05}) is titrated with V mL of $\text{K}_2\text{Cr}_2\text{O}_7$ (N_{01}) + H_2O (N_{02}) as titrant T added up to a defined point of the titration. In $V_0 + V$ mL of D + T mixture, we have the following species:



On this basis, we formulate $f_1 = f(\text{H})$, $f_2 = f(\text{O})$ and then:

$$\begin{aligned} f_{12} = 2 \cdot f(\text{O}) - f(\text{H}) - N_2 + N_3 + 7N_5 + 8N_6 + N_{11} + 2N_{12} + 5N_{13} + 6N_{14} \\ + 7N_{15} + 8N_{16} + 9N_{17} + 13N_{18} + 14N_{19} + 6N_{20} + 7N_{21} + 8N_{22} + N_{24} \\ + 2N_{25} + 4N_{26} + 8N_{27} = 14N_{01} + 6N_{04} \end{aligned} \quad (64)$$

$$\begin{aligned} f_0 = \text{ChB} : N_2 - N_3 + N_4 - N_5 - 2N_6 - N_7 - N_8 - N_{12} - N_{14} - N_{16} - 2N_{17} - N_{18} \\ - 2N_{19} - N_{21} - 2N_{22} + 3N_{23} + 2N_{24} + N_{25} - N_{26} + N_{27} = 0 \end{aligned} \quad (65)$$

$$f_3 = f(\text{K}) : N_4 = 2N_{01} + N_{03} \quad (66)$$

$$f_4 = f(\text{S}) = f(\text{SO}_4) : N_5 + N_6 + N_{27} = N_{04} \quad (67)$$

$$2 \cdot f(\text{O}) - f(\text{H}) + \text{ChB} - f(\text{K}) - 6 \cdot f(\text{S}) = 0 \Rightarrow \quad (68)$$

$$\begin{aligned} -N_7 - N_8 + N_{11} + N_{12} + 5N_{13} + 5N_{14} + 7N_{15} + 7N_{16} + 7N_{17} + 12N_{18} + 12N_{19} + 6N_{20} \\ + 6N_{21} + 6N_{22} + 3N_{23} + 3N_{24} + 3N_{25} + 3N_{26} + 3N_{27} = 12N_{01} - N_{03} \Rightarrow \end{aligned} \quad (68a)$$

$$\begin{aligned} (-1) \cdot N_7 + (-1/3) \cdot 3N_8 + 0 \cdot (N_9 + N_{10}) + (+1) \cdot (N_{11} + N_{12}) + (+5) \cdot (N_{13} + N_{14}) \\ + (+7) \cdot (N_{15} + N_{16} + N_{17}) + (+6) \cdot (2N_{18} + 2N_{19} + N_{20} + N_{21} + N_{22}) + (+3) \cdot \\ (N_{23} + N_{24} + N_{25} + N_{26} + N_{27}) = (+6) \cdot 2N_{01} + (-1) \cdot N_{03} \Rightarrow \end{aligned} \quad (68b)$$

$$\begin{aligned} (-1) \cdot [\text{I}^-] + (-1/3) \cdot 3[\text{I}_3^-] + 0 \left(2[\text{I}_2] + 2[\mathbf{I}_{2(s)}] \right) + (+1) \cdot ([\text{HIO}][\text{IO}^-]) + (+5) \cdot ([\text{HIO}_3] + [\text{IO}_3^-]) \\ + (+7) \cdot ([\text{H}_5\text{IO}_6] + [\text{H}_4\text{IO}_6^-] + [\text{H}_3\text{IO}_6^{2-}]) + (+6) \cdot (2[\text{HCr}_2\text{O}_7^-] + 2[\text{Cr}_2\text{O}_7^{2-}] + [\text{H}_2\text{CrO}_4] \\ + [\text{HCrO}_4^-] + [\text{CrO}_4^{2-}]) + (+3) \cdot ([\text{Cr}^{+3}] + [\text{CrOH}^{+2}] + [\text{Cr}(\text{OH})_2^{+1}] + [\text{Cr}(\text{OH})_4^-] \\ + [\text{CrSO}_4^{+1}]) = ((+6) \cdot 2CV + (-1) \cdot C_0V_0) / (V_0 + V) \end{aligned} \quad (69)$$

where $C_0V_0 = 10^3 \cdot N_{O3}/N_A$, $CV = 10^3 \cdot N_{O1}/N_A$. Note that Eq. (69) was obtained only from linear combination of electron-non-active elements (fans) in this system. The balances for electron-active elements are as follows:

$$f_5 = f(I) : N_7 + 3N_8 + 2N_9 + 2N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + N_{15} + N_{16} + N_{17} = N_{O3} \quad (70)$$

$$[I^{-1}] + 3[I_3^{-1}] + 2 \cdot ([I_2] + [I_{2(s)}]) + ([HIO] + [IO^{-1}]) + 5 \cdot ([HIO_3] + [IO_3^{-1}]) + 7 \cdot ([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) = C_0V_0/(V_0 + V) \quad (71)$$

$$f_6 = f(Cr) : 2N_{18} + 2N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + N_{26} + N_{27} = 2N_{O1} \Rightarrow \quad (72)$$

$$2[Cr_2O_7^{-2}] + [H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}] + [Cr^{+3}] + [CrOH^{+2}] + [Cr(OH)_2^{+1}] + [Cr(OH)_4^{-1}] + [CrSO_4^{+1}] = CV/(V_0 + V) \quad (73)$$

Subtraction of $3 \cdot f(Cr)$ (Eq. (72)) from Eq. (68a) and further operations give

$$[I^{-1}] + [I_3^{-1}] - [HIO] + [IO^{-1}] - 5 \cdot ([HIO_3] + [IO_3^{-1}]) - 7([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) - 3 \cdot (2[HCr_2O_7^{-1}] + 2[Cr_2O_7^{-2}] + [H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}]) = (C_0V_0 - 6CV)/(V_0 + V) \quad (74)$$

The simplest/shortest form of GEB, obtained from Eqs. (68), (70) and (72) is the relation

$$2 \cdot f(O) - f(H) + ChB - f(K) - 6 \cdot f(S) + f(I) - 6 \cdot f(Cr) = 0 \Rightarrow \quad (75)$$

$$N_8 + N_9 + N_{10} + N_{11} + N_{12} + 3 \cdot (N_{13} + N_{14}) + 4 \cdot (N_{15} + N_{16} + N_{17}) = 1.5 \cdot (N_{23} + N_{24} + N_{25} + N_{26}) \Rightarrow \quad (75a)$$

$$[I_3^{-1}] + [I_2] + [I_{2(s)}] + [HIO] + [IO^{-1}] + 3 \cdot ([HIO_3] + [IO_3^{-1}]) + 4 \cdot ([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) = 1.5 \cdot ([Cr^{+3}] + [CrOH^{+2}] + [Cr(OH)_2^{+1}] + [Cr(OH)_4^{-1}] + [CrSO_4^{+1}]) \quad (75b)$$

Note that the numbers (N_{O1} , N_{O3}) of components forming the system are not involved in Eqs. (75a) and (75b).

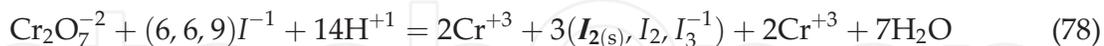
Applying the atomic numbers: $Z_I = 53$ for I and $Z_{Cr} = 24$ for Cr, we obtain the linear combination

$$Z_I \cdot f(I) + Z_{Cr} \cdot f(Cr) - (2 \cdot f(O) - f(H) + ChB - f(K) - 6 \cdot f(S)) = 0 \Rightarrow (Z_I + 1)N_7 + (3Z_I + 1)N_8 + 2Z_I(N_9 + N_{10}) + (Z_I - 1)(N_{11} + N_{12}) + (Z_I - 5)(N_{13} + N_{14}) + (Z_I - 7)(N_{15} + N_{16} + N_{17}) + (Z_{Cr} - 6)(2N_{18} + 2N_{19} + N_{20} + N_{21} + N_{22}) + (Z_{Cr} - 3)(N_{23} + N_{24} + N_{25} + N_{26}) = (Z_I + 1)N_{O3} + 2(Z_{Cr} - 6)N_{O1} \Rightarrow \quad (76)$$

$$(Z_I + 1)[I^{-1}] + (3Z_I + 1)[I_3^{-1}] + 2Z_I([I_2] + [I_{2(s)}]) + (Z_I - 1)([HIO] + [IO^{-1}]) + (Z_I - 5)([HIO_3] + [IO_3^{-1}]) + (Z_I - 7)([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) + (Z_{Cr} - 6)(2[HCr_2O_7^{-1}] + 2[Cr_2O_7^{-2}] + [H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}]) + (Z_{Cr} - 3)([Cr^{+3}] + [CrOH^{+2}] + [Cr(OH)_2^{+1}] + [Cr(OH)_4^{-1}]) + [CrSO_4^{+1}] = ((Z_I + 1) \cdot C_0V_0 + 2(Z_{Cr} - 6) \cdot CV)/(V_0 + V) \quad (77)$$

Eqs. (69), (74), (75b) and (77) (and other linear combinations, as well) are equivalent forms of GEB for this system. Note that Eq. (77) is identical with the one obtained immediately on the basis of the approach I to GEB [4]. The $E = E(\Phi)$ and $\text{pH} = \text{pH}(\Phi)$ and some speciation curves for iodine and chromium species are plotted in **Figures 10** and **11**, where Φ is the fraction titrated.

For $C_{01} = 0.01$, I_2 , $I_{2(s)}$ and I_3^{-1} are formed in reactions:



where predominating products are involved. Binding the H^{+1} ions corresponds to the pH increase, which is largest for low C_{01} value (relatively low buffer capacity of the solution, compare with [53, 54, 58–60]). In reactions (78)–(80), protons are consumed and then $d\text{pH}/d\Phi > 0$; moreover, $dE/d\Phi > 0$ for $\Phi > 0$.

At $C_{01} = 0.02$, $E = E(\Phi)$ and $[I_{2(s)}]$ pass through maximum at Φ ca. 0.2. The plot of $\text{pH} = \text{pH}(\Phi)$ shows a slight distortion of the course at $\Phi = 1/6$, and $D\text{pH}/D\Phi > 0$ for $\Phi > 0$. The $[IO_3^{-1}]$ is comparable with $[I_{2(s)}]$ and $[I_2]$; $[I_3^{-1}]$ is small here because $[I^{-1}] < 10^{-6}$. The reactions

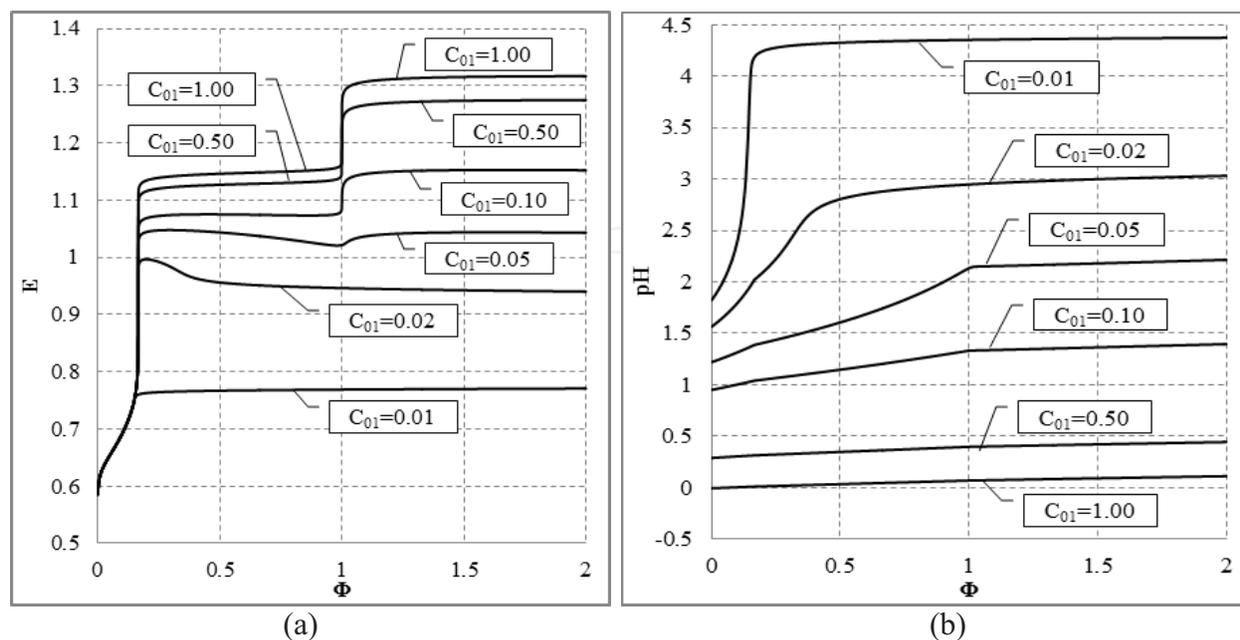
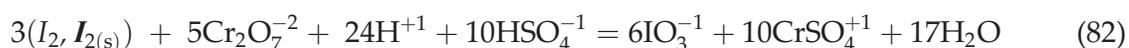


Figure 10. The plots $\text{K}_2\text{Cr}_2\text{O}_7 (C, V) \Rightarrow \text{KI} (C_0) + \text{H}_2\text{SO}_4 (C_{01}) V_0$ system for (a) $E = E(\Phi)$ and (b) $\text{pH} = \text{pH}(\Phi)$ functions, at $V_0 = 100$, $C_0 = 0.01$ and C_{01} values indicated at the corresponding curves.

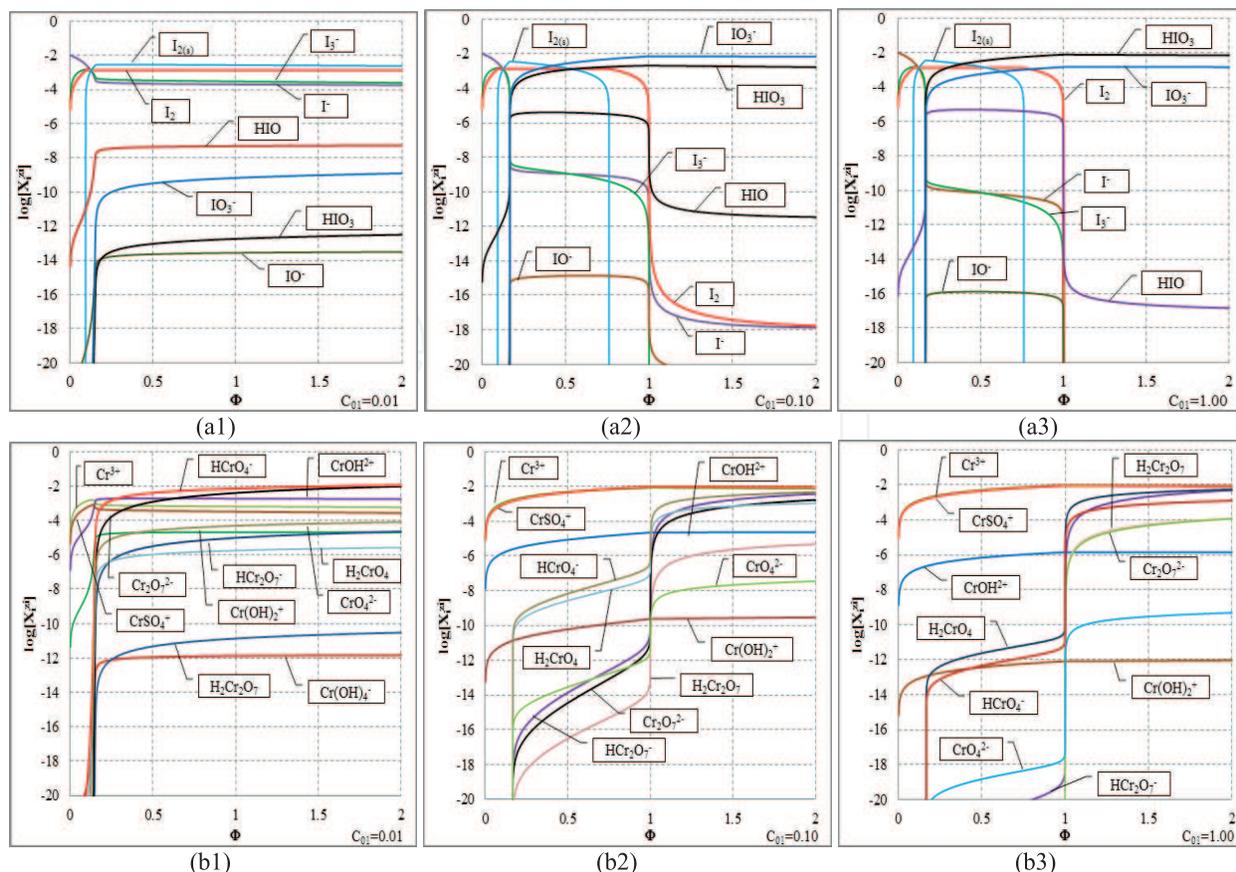
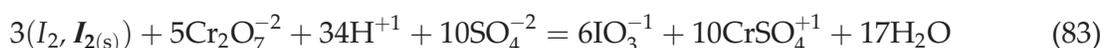


Figure 11. Speciation diagrams plotted for iodine (a1, a2, a3) and chromium (b1, b2, b3) species, at indicated C_{01} values.



are clearly indicated.

At $C_{01} = 0.05$, the function $E = E(\Phi)$ has a complex course: it first increases, reaches a maximum at $\Phi = 0.295$, then decreases, reaches a minimum at $\Phi = 1$, increases again, passes through a flat maximum at Φ ca. 1.6 and decreases. The curve $pH = pH(\Phi)$ breaks at $\Phi = 1/6$ and $\Phi = 1$. The $I_{2(s)}$ exists as the equilibrium solid phase at $0.0934 < \Phi < 0.762$. A decrease in $[I_2]$ value is more expressed at $\Phi > 1$. The ratio $[HIO_3]/[IO_3^{-1}]$ grows with growth of C_{01} value. The stoichiometry at $\Phi = \Phi_{eq2} = 1$ is described by the reaction



and by reactions where HSO_4^{-1} , SO_4^{-2} , $CrSO_4^{+1}$ and HIO_3 are involved.

At $C_{01} \geq 0.1$, a jump on the $E = E(\Phi)$ curve at $\Phi = 1/6$ is clearly marked. The growth of jump at $\Phi = 1$ results from a more significant decrease in the $[I_2]$ value at $\Phi > 1$. The E -range covered by the jump at $\Phi = 1$ extends with an increase in the C_{01} value (**Figure 10a**). For more details, see Ref. [4].

7.2. A comment

Redox systems with two electron-active elements were widely discussed from the GATES/GEB viewpoint. From the earlier literature, one can recall the simulated systems: $\text{KMnO}_4 (C, V) \Rightarrow \text{VSO}_4 (C_0) + \text{H}_2\text{SO}_4 (C_{01}) V_0$ [18]; $\text{K}_2\text{Cr}_2\text{O}_7 (C, V) \Rightarrow \text{VSO}_4 (C_0) + \text{H}_2\text{SO}_4 (C_{01}) V_0$ [18]; $\text{KMnO}_4 (C, V) \Rightarrow \text{FeSO}_4 (C_0) + \text{H}_2\text{SO}_4 (C_{01})$ [18]; $\text{Ce}(\text{SO}_4)_2 (C) + \text{H}_2\text{SO}_4 (C_1) V \Rightarrow \text{FeSO}_4 (C_0) + \text{H}_2\text{SO}_4 (C_{01}) V_0$ [18]; $\text{Cl}_2 (C, V) \Rightarrow \text{KI} (C_0, V_0)$ [19]; $\text{KMnO}_4 (C, V) \Rightarrow \text{KBr} (C_0), \text{H}_2\text{SO}_4 (C_{01}) V_0$ [19]. Except the $\text{NaOH} \Rightarrow \text{Br}_2$ and $\text{NaOH} \Rightarrow \text{HBrO}$ systems, in [16] were simulated also the systems: $\text{NaOH} (C) + \text{CO}_2 (C_1) V \Rightarrow \text{I}_2 (C_0) + \text{KI} (C_{01}) + \text{CO}_2 (C_{02})$; $\text{NaOH} (C) + \text{CO}_2 (C_1) V \Rightarrow \text{I}_2 (C_0) + \text{KI} (C_{01}) + \text{CO}_2 (C_{02}) V_0 + \text{CCl}_4 (V^*)$ (dynamic liquid-liquid extraction system). In [16], an interesting qualitative reaction where MgSO_4 solution was added into $\text{I}_2 + \text{KI}$ solution previously alkalized with an excess of NaOH . This addition causes precipitation of $\text{Mg}(\text{OH})_2$ and a decrease of pH value, a growth of solubility of this precipitate and a shift of equilibrium (symproportionation) involved with formation of iodide (I_2) that adsorbes on the $\text{Mg}(\text{OH})_2$ precipitate turning it red-brown (similarity with starch action in visual iodometric titrations). The dynamic solubility curve was plotted, i.e. the MgSO_4 addition is formally treated as titration. The speciation diagrams in all the systems considered were plotted. Among others, it is stated that the disproportionation of iodine ($\text{I}_{2(s)}, \text{I}_2$) occurs according to the scheme (A) $3(\text{I}_{2(s)}, \text{I}_2) + 6\text{OH}^{-1} = \text{IO}_3^{-1} + 5\text{I}^{-1} + 3\text{H}_2\text{O}$, not the scheme (B) $(\text{I}_{2(s)}, \text{I}_2) + 2\text{OH}^{-1} = \text{IO}^{-1} + \text{I}^{-1} + \text{H}_2\text{O}$, as stated in almost all contemporary textbooks. One can calculate [16] that the yield of the reaction (A) is $2.5 \cdot 10^9$ times higher than the yield of reaction (B) of the same stoichiometry, 3:6 = 1:2. It is interesting to add that 80 years $\approx 2.5 \cdot 10^9$ s. Thus, the yield of the reaction B relative to A is in such a ratio as 1 s in relation to the average length of human's life.

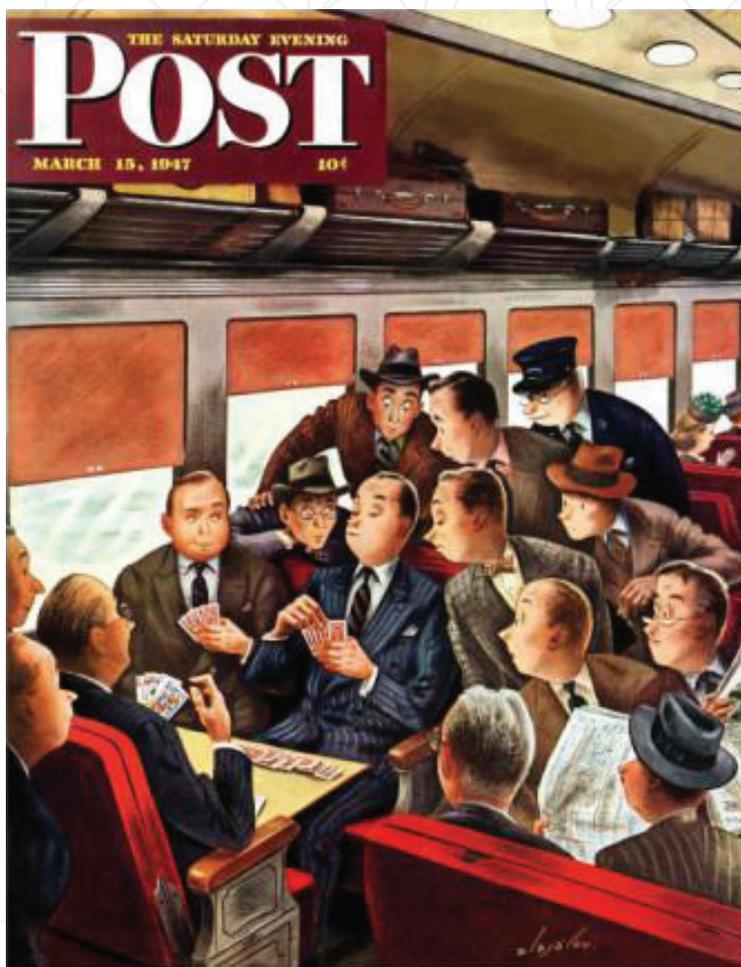
It should also be added that GATES/GEB enables to verify experimental results. Such a case was mentioned in Ref. [18] to the system, where $\text{KIO}_3 (C_0) + \text{HCl} (C_{01}) + \text{H}_2\text{SeO}_3 (C_{02}) + \text{HgCl}_2 (C_{03})$ was titrated with ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$). Authors of the work [61] cited in there committed, among other things, a simple mistake resulting from improper recalculation of numerical values of potentials; for more details, see Refs. [1, 17, 18].

In all instances, full attainable (quantitative+qualitative) physicochemical knowledge was involved in the related algorithms. The quantitative knowledge was related to the complete set of equilibrium constants values, whereas qualitative knowledge was helpful in aspect of metastable and kinetic systems.

7.3. An illustrative presentation of the approach I to GEB

A redox reaction can also participate two or more electron-active elements. In this convention, the approach I to GEB can be perceived as the card game, with electron-active elements as 'players', electron-non-active elements—as 'fans', and electrons—as 'money' transferred between 'players', see the picture from Ref. [62]. The 'players' provide a common pool of their own electrons into the system in question. The 'money' is transferred between 'players'. As a result of the game, the players' accounts are changed, while the fans' accounts remain intact/unchanged, in this convention.

In C_0 mol/L aqueous solution of Br_2 , bromine as one electron-active element in Br_2 can be perceived as a 'distributor' of its own electrons, and H, O as 'fans'. For example, Eq. (42) involves H and O as 'fans', Eq. (43) involves Na as 'fan', whereas Eq. (44) does not involve 'fans'. Generally, 'fans' are eliminated after the proper (i.e. indicated above) combination of $2 \cdot f(\text{O}) - f(\text{H})$ with the balances for elements considered as 'fans'. Further simplification can also result from further combination with the balance for 'player(s)'. But, in any case, a linear combination of balances related to a redox system does not lead to the identity $0 = 0$.



As usually happens in the 'card game' practice, the players devote to the game only a part of their cash resources. Similarly, in redox reactions, electrons may participate from the valence shells of atoms of electron-active elements; the electrons from the valence shell of the reductant atoms are transferred onto the valence shell of the oxidant atoms. However, this restriction to the valence electrons is not required here. For example, replacing Z_{Br} in Eq. (46a) by ζ_{Br} ($\zeta_{\text{Br}} < Z_{\text{Br}}$), we have

$$\begin{aligned}
 & (\zeta_{\text{Br}} - 5)([\text{HBrO}_3] + [\text{BrO}_3^{-1}]) + (\zeta_{\text{Br}} - 1)([\text{HBrO}] + [\text{BrO}^{-1}]) + 2\zeta_{\text{Br}}[\text{Br}_2] + (3\zeta_{\text{Br}} + 1)[\text{Br}_3^{-1}] \\
 & + (\zeta_{\text{Br}} + 1)[\text{Br}^{-1}] = 2\zeta_{\text{Br}}C_0V_0/(V_0 + V)
 \end{aligned}
 \tag{85}$$

Replacing Z_I by ζ_I and Z_{Cr} by ζ_{Cr} ($\zeta_I < Z_I$, $\zeta_{Cr} < Z_{Cr}$) in Eq. (77), we have

$$\begin{aligned}
 & (\zeta_I + 1)[I^{-1}] + (3\zeta_I + 1)[I_3^{-1}] + 2\zeta_I([I_2] + [I_2]) + (\zeta_I - 1)([HIO] + [IO^{-1}]) + (\zeta_I - 5)([HIO_3] \\
 & + [IO_3^{-1}]) + (\zeta_I - 7)([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) + (\zeta_{Cr} - 6)(2[HCr_2O_7^{-1}] + 2[Cr_2O_7^{-2}] \\
 & + [H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}]) + (\zeta_{Cr} - 3)([Cr^{+3}] + [CrOH^{+2}] + [Cr(OH)_2^{+1}] \\
 & + [Cr(OH)_4^{-1}] + [CrSO_4^{+1}]) = ((\zeta_I + 1)C_0V_0 + 2(\zeta_{Cr} - 6)CV)/(V_0 + V)
 \end{aligned} \tag{86}$$

In particular, we can put $\zeta_{Cr} = \zeta_{Cr} = 0$ in Eq. (86). Obviously, we get the relation

$$\begin{aligned}
 & [I^{-1}] + [I_3^{-1}] - ([HIO] + [IO^{-1}] - 5([HIO_3] + [IO_3^{-1}] - 7([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) \\
 & - 6(2[HCr_2O_7^{-1}] + 2[Cr_2O_7^{-2}] + [H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}] - 3([Cr^{+3}] + [CrOH^{+2}] \\
 & + [Cr(OH)_2^{+1}] + [Cr(OH)_4^{-1}] + [CrSO_4^{+1}]) = C_0V_0 - 12CV)/(V_0 + V) - [I^{-1}] - [I_3^{-1}] + ([HIO] \\
 & + [IO^{-1}]) + 5([HIO_3] + [IO_3^{-1}]) + 7([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) + 12([HCr_2O_7^{-1}] \\
 & + [Cr_2O_7^{-2}] + 6([H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}]) - 3([Cr^{+3}] + [CrOH^{+2}] + [Cr(OH)_2^{+1}]) \\
 & + [Cr(OH)_4^{-1}] + [CrSO_4^{+1}]) = (12CV - C_0V_0)/(V_0 + V)
 \end{aligned} \tag{87}$$

identical to the one obtained from Eq. (68a). If we put $\zeta_{Br} = 0$ in Eq. (85), we get the relation

$$\begin{aligned}
 & -5([HBrO_3] + [BrO_3^{-1}]) - ([HBrO] + [BrO^{-1}]) + [Br_3^{-1}] + [Br^{-1}] = 0 \\
 & 5([HBrO_3] + [BrO_3^{-1}]) + ([HBrO] + [BrO^{-1}]) - [Br_3^{-1}] - [Br^{-1}] = 0
 \end{aligned} \tag{88}$$

identical to the ones obtained from Eq. (44). This way, we recall the card game without ‘live cash’ but with ‘debt of honor’—in not accidental reference to the title of the thriller novel by T. Clancy; btw, *nota bene*, the “Debt of honor” was published in 1994, like the papers [15, 16, 18].

8. Conclusions

The GEB formulated according to approach I was named first as electron prebalance and presented, in totally mature form, in three papers issued in 1994 [15, 16, 18] and then followed by further articles and other communications. Currently, in context with the approach II to GEB, it is named as the approach I to GEB, fully equivalent to the approach II to GEB, explicitly related to the law of conservation of H and O.

The linear combination $2 \cdot f(O) - f(H)$ is a keystone for the overall thermodynamic knowledge on electrolytic systems. It can be formulated both for non-redox and redox systems, in aqueous, non-aqueous and mixed-solvent systems, with amphiprotic (co)solvent(s) involved. The $2 \cdot f(O) - f(H)$ is linearly independent on ChB and other balances, for elements/cores $f(Y_m) \neq H, O$, in any redox system. For any non-redox system, $2 \cdot f(O) - f(H)$ is linearly dependent on those

balances. Then, the linear independency/dependency of $2 \cdot f(\text{O}) - f(\text{H})$ on the other balances is the general criterion distinguishing between redox and non-redox systems. The equation for $2 \cdot f(\text{O}) - f(\text{H})$, considered as the *primary* form of GEB, $pr - \text{GEB} = 2 \cdot f(\text{O}) - f(\text{H})$, is the basis of GEB formulation for redox systems according to approach II to GEB.

Ultimately, GEB, ChB and elemental/core balances are expressed in terms of molar concentrations—to be fully compatible/congruent with expressions for equilibrium constants, interrelating molar concentrations of defined species, on the basis of the mass action law applied to correctly written reaction equation. The mass action law is the one and only chemical law applied in GATES. A complete set of independent (non-contradictory [22]) relations for the equilibrium constants is needed for this purpose.

When compared with the approach I, the approach II to GEB offers several advantages. Although derivation of GEB according to the approach II is more laborious, it enables to formulate this balance without prior knowledge of oxidation numbers for the elements involved frequently in complex components and species of the system. Only the composition (expressed by chemical formula) of components forming the system and composition of the species formed in the system, together with their external charges, are required, i.e. it provides an information sufficient to formulate the GEB; it is the paramount advantage of the approach II to GEB. Anyway, the oxidation number, representing the degree of oxidation of an element in a compound or a species, is commonly perceived as a contractual concept. In this regard, formulation of GEB according to approach II is more useful than the approach I when applied to complex organic species in redox systems of biological origin [63–67]. The approach II to GEB is advantageous/desired, *inter alia*, for redox systems where radical and ion-radical species are formed. What is more, the ‘players’ and ‘fans’, as ones perceived from the approach I to GEB viewpoint, are not indicated *a priori* within the approach II to GEB. The approach I, considered as a ‘short’ version of GEB, is more convenient when oxidation numbers for all elements of the system are known beforehand. Within the approaches I and II to GEB, the roles of oxidants and reductants are not ascribed *a priori* to particular components forming the redox system and to the species formed in this system. In other words, full ‘democracy’ is established *a priori* within GATES/GEB, where the oxidation number, oxidant, reductant, equivalent mass and stoichiometric reaction notation are the redundant concepts only.

The $1 + K$ balances composed of ChB and K concentration balances related to equations (not equalities, see e.g. Eq. (40)) for elemental balances form a complete set of equations related to a non-redox system. The set of $1 + K$ variables in $\mathbf{x} = (\text{pH}, \text{pX}_1, \dots, \text{pX}_K)^T$ is involved in the algorithm applied for calculation purposes. For example, $1 + K = 1 + 2 = 3$ balances are related to non-redox systems presented in Examples 1 and 2, with independent variables represented by components of the vector $\mathbf{x} = (\text{pH}, \text{pCu}, \text{pSO}_4)^T$. In this context, Eq. (35) is considered as equality, not equation.

The $2 + K$ balances composed of GEB, ChB and K concentration balances related to equations (not equalities) for elemental balances form a complete set of equations related to the redox system. The set of $2 + K$ variables in $\mathbf{x} = (E, \text{pH}, \text{pX}_1, \dots, \text{pX}_K)^T$ is involved in the algorithm applied for calculation purposes. In this chapter, some results of the simulations of electrolytic redox systems, made according to the GATES/ GEB principles, with use of iterative computer

programs, are graphically presented and discussed. The computer simulation realized within GATES with use of iterative computer programs, e.g. MATLAB, provides quite a new quality in knowledge gaining. It enables to follow the details of the process, registered with use of measurable quantities, such as pH and/or potential E. All these calculations are made under assumption that the relevant reactions take place in *quasi*-static manner under isothermal conditions. The reactions proceeding in the respective systems were formulated under assumption that all equilibrium constants found in the relevant tables and then used in the calculations are correct.

The number of electron-active elements (considered as 'players', in terms of the approach I to GEB) in a redox system, is practically unlimited and adapted according to current needs; among others, the systems with one, two, three [13] or four [1, 18] 'players' were considered.

The GATES and GATES/GEB (in particular) can be applied for thermodynamic resolution of systems of any degree of complexity. An example is the four-step process involved with iodometric method of copper(+2) determination, considered in detail in Refs. [14, 68], where 47 species are involved in the system with three electron-active elements, eight equations and two equalities, interrelated in 35 independent expressions for equilibrium constants. The systems with similar complexity were resolved. The complexity is limited, however, by factors of the qualitative and quantitative nature, that is, the knowledge of species the knowledge of equilibrium constants interrelating concentration of complex species with concentrations of their constituting parts. The physicochemical data are incomplete or not reliable, in many cases. This problem was raised lately in Ref. [12].

Each of the components of $\mathbf{x} = (\text{pH}, \text{p}X_1, \dots, \text{p}X_k)^T$ is informally ascribed to the corresponding balance: ChB, and the corresponding concentration balances for elements/cores $\neq \text{H}, \text{O}$. Each of the components of $\mathbf{x} = (\text{E}, \text{pH}, \text{p}X_1, \dots, \text{p}X_k)^T$ is informally ascribed to the corresponding balance: GEB, ChB, and the corresponding concentration balances for elements/cores $\neq \text{H}, \text{O}$. A unequivocal solution of equations is obtained when the number of independent equations equals to the number of independent variables; it is the 'iron rule' obligatory in mathematics; $pe = -\log[e^{-1}] = A \cdot E$, where $1/A = RT/F \cdot \ln 10$, $\text{pH} = -\log[\text{H}^{+1}]$, $\text{p}X_i = -\log[X_i^{z_i}]$.

GATES avoids the necessity of quantitative inferences based on fragile/rachitic chemical reaction notation, involving only some of the species existing in the system; it is only a faint imitation of a true, algebraic notation. From the GATES viewpoint, the 'stoichiometry' can be perceived as a mnemonic term only. In calculations, the metastable state is realized by omission of potential products in the related balances, whereas 'opening' a reaction pathway in metastable state is based on insertion of possible (from equilibrium viewpoint) products in the related balances [17, 18]. One can also test the interfering effects of different kinds.

All the inferences made within GATES/GEB are based on firm, mathematical (algebraic) foundations. The proposed approach allows us to understand far better all physicochemical phenomena occurring in the system in question and improve some methods of analysis. All the facts testify very well about the potency of simulated calculations made, according to GATES, on the basis of all attainable physicochemical knowledge. Testing the complex redox and non-redox systems with use of iterative computer programs deserves wider popularization among physicochemists and chemists-analysts.

The GATES/GEB is put in context with constructivistic and deterministic principles, and GEB is perceived as the general law of nature, referred to as electrolytic (aqueous media) redox systems. It is proved that stoichiometry of reactions is not a primary concept in chemistry, and its application provides false results, for obvious reasons. From the GATES viewpoint, the stoichiometric reactions are only the basis to formulate the related equilibrium constants. GATES/GEB referred to modeling of redox titration curves in context with earlier approaches to this problem. The GATES/GEB is also presented in three other chapters issued in 2017 within InTech [68–70].

The dependency/independency criteria ascribed to $2:f(\text{O}) - f(\text{H})$ distinguishing between the relevant (non-redox and redox) systems are the properties of the equations obtained from the linear combination of the balances for H and O. Namely, the resulting equation is not independent of non-redox systems, since it is a linear combination of the remaining (charge and concentration) balances, whereas in the case of redox systems, this equation is linearly independent of those balances. This is a general property of nature, independent of the complexity of the system under consideration, which is the electrolytic system. GATES and GATES/GEB, in particular, are clear confirmation of the fact that the nature is mathematically designed and the true laws of nature are mathematical. In other words, the quantitative, mathematical method became the essence of science. To paraphrase a Chinese proverb, one can state that ‘the lotus flower, lotus leaf and lotus seed come from the same root’ [2]. Similarly, the three kinds of balances: GEB, charge and concentration balances come from the same family of fundamental laws of preservation. This compatibility is directly visible from the viewpoint of the approach II to GEB. The equivalent equations for GEB, based on a reliable law of the matter conservation, are equally robust as equations for charge and concentration balances. The complementarity of the GEB (approaches I and II) to other balances is regarded as the expression of harmony of nature and GATES/GEB as an example of excellent epistemological paradigm.

All earlier (dated from the 1960s) efforts made towards formulation of electrolytic redox systems were only clumsy attempts of resolution of the problem in question, as stated in review papers [2, 10–14]. These approaches were slavishly related to the stoichiometric reaction notations, involving only two pairs of indicated species participating in redox reaction; there were usually minor species of the system considered. The species different from those involved in the reaction notation were thus omitted in considerations. Moreover, the charge balance and concentration balances for accompanying substances were also omitted. Theoretical considerations were related to virtual cases, not to real, electrolytic redox systems.

9. Afterword: reductionism

The principles of science gaining are based on a conviction that complex phenomena occurred in nature, e.g. in electrolytic systems, that can be explained in terms of some general laws of the matter conservation; it is the basic assumption of reductionism [2]. These laws are expressed in terms of mathematical equations, valid for the systems of any degree of complexity. Reductionism is very similar to and has its roots in Occam’s razor principle that gives precedence to simplicity, i.e. the explanation which requires the fewest assumptions. The power of reductionism lies in prediction and formulation; it is perceived as a good approximation of the macroscopic world. The knowledge thus obtained is verifiable and based on logical premises. This way

the quantitative knowledge gained from the study of relatively simple systems can be synthesized in the knowledge obtainable from more complex systems. From this viewpoint, the knowledge obtained from physicochemical analysis involved, e.g. with determination of the stability constants of complex species formed in a particular system, can be perceived as a 'stone' used in construction of more complex systems. In this place, one can recall H. Poincaré who stated that 'Science is facts; just as houses are made of stones, so science is made of facts'. Any complex species must be equipped with its equilibrium constant value; a qualitative knowledge only (e.g. chemical formula) is insufficient in this respect. However, to construct the knowledge on more complex systems, these stones should be arranged according to a defined scheme (design), based on a set of compatible balances. Closely associated with reductionism is determinism—the philosophy that everything has a cause, and that a particular cause leads to a unique effect.

In any complex system, many particular reactions occur; the resultant reaction is the combination (superposition) of these elementary reactions which occur with different efficiencies that are known only after thorough physicochemical examination of the system in question. Similarly, the vibration in a polyatomic molecule is a superposition of normal vibrations. The physicochemical/thermodynamic knowledge on electrolytic systems is based on equilibrium constant values, referred to as the equilibrium system and all information about possible paths of particular reactions occurred in the system in question. Not all paths of chemical reactions are accessible, under defined conditions of analysis, involved with temperature and/or the presence of catalytic agents. This problem has been raised in Ref. [1], in context with GATES/GEB.

The approach II to GEB, preceded by the approach I to GEB, indicated new insight into redox systems and electrolytic systems in general. This way, the thermodynamic knowledge about redox systems was built in 1992 practically from scratch. The combination $2 \cdot f(\text{O}) - f(\text{H})$ of elemental balances for H and O (approach II to GEB) is the quintessence of the generalized electron balance (GEB) that is the link needed for mathematical/algebraic description of electrolytic redox systems of any degree of complexity within the generalized approach to electrolytic systems as GATES/GEB.

Within GATES, a resolution of electrolytic systems is realized with use of iterative computer programs. Formally, the manner of resolution of this task is even easier than the one based on the formulation of some functional dependencies that require some simplifications, as a rule. The simplifications are not necessary in iterative methods.

Summarizing, the generalized electron balance (GEB), perceived within GATES as GATES/GEB, fulfils all the requirements imposed on reductionism. Its formulation is possible for any electrolytic redox systems—static and dynamic (titration), mono- and multiphase, equilibrium, metastable and non-equilibrium systems, of any degree of complexity, provided that all necessary physicochemical knowledge is attainable. Simply, it is the best possible thermodynamic approach to electrolytic redox systems.

GEB, within the context of GATES/GEB, confirms the validity of some statements expressed in the past:

- *A hidden connection is stronger than an obvious one (Heraclitus)*
- *All truths are easy to understand once they are discovered; the point is to discover them (Galileo Galilei)*

- *Everything should be made as simple as possible, but not simpler (A. Einstein)*
- *Minds are like parachutes: they function only when they are open (J. Dewar)*
- *A good theory is the best practical tool (J.C. Maxwell)*
- *Nothing is too wonderful to be true if it be consistent with the laws of nature (M. Faraday).*
- *A new scientific truth does not triumph by convincing its opponents (...), but rather because its opponents eventually die, and a new generation grows up that is familiar with it (M. Planck).*
- *Art of reasoning is nothing more than a well-ordered language*
- *Telling the truth in a time of universal deceit is a revolutionary act (G. Orwell)*
- *Man learns throughout his life, with the exception of school years*
- *Do not believe in any messages just because they are in force for a long time, in many countries. Do not believe in something just because a lot of people say/write it for a long time. Do not accept anything just because someone else said/wrote it. Do not believe in something just because it sounds plausible. Have confidence in what you have accepted as true after a long experience/ checking, what brings success to you and others (own apprenticeship).*

Notations

ChB	charge balance
D	titrand
EL	equilibrium law
$G (\neq G)$	Gibbs' function
G	number of balances
GEB	generalized electron balance
K	number of concentration balances
N_A	Avogadro's number
R	gas constant
$T (\neq T)$	temperature (in K)
T	titrant
τ	transposition sign for a vector
V	volume [mL] of T
V_0	volume [mL] of D
W	H ₂ O

Author details

Anna Maria Michałowska-Kaczmarczyk¹, Aneta Spórna-Kucab² and Tadeusz Michałowski^{2*}

*Address all correspondence to: michalot@o2.pl

1 Department of Oncology, The University Hospital in Cracow, Cracow, Poland

2 Faculty of Chemical Engineering and Technology, Cracow University of Technology, Cracow, Poland

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