



Research Article

Formulation of Simple Electrolytic Redox Systems According to GATES/GEB Principles

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Abstract

The linear combination $f_{12} = 2 \cdot f(O) - f(H)$ of elemental balances: $f_1 = f(H)$ for H, and $f_2 = f(O)$ for O is the basis to formulate the generalized electron balance (GEB) for electrolytic redox systems according to Approach II to GEB, realized within the generalized approach to electrolytic systems (GATES) as GATES/GEB. Together with charge balance ($f_0 = ChB$) and $K-2$ elemental/core balances: f_3, \dots, f_K , the f_{12} completes the set of K balances needed for resolution of an electrolytic redox system, of any degree of complexity. For a non-redox system, a proper linear combination of f_{12} with f_0 , and $f_k = f(Y_k)$ ($Y_k \neq H, O$; $k=3, \dots, K$) gives the identity, $0 = 0$. Consequently, in non-redox systems, f_{12} is linearly dependent on f_0, f_3, \dots, f_K , i.e., f_{12} is not the independent balance. This independency/dependency property of f_{12} distinguishes between redox and non-redox systems. In a redox system, a proper linear combination of $f_{12} + f_0$ with the balances for electron-non-active elements/cores gives the simpler form of GEB, where the species composed only of electron-non-active elements are not involved. The multipliers applied in the linear combinations are equal to the oxidation numbers for elements participating redox or non-redox system. This regularity is highly important in context of the fact that the 'oxidation number' was essentially a contractual concept. Within GATES/GEB, the terms: oxidation number, oxidant and reductant, stoichiometry, and equivalent mass are derivative/redundant concepts only; the roles of oxidants and reductants are not assigned *a priori* to individual components. All these concepts are illustrated on simple examples of redox D+T systems, with aqueous solutions of (S1) Br_2 , and (S2) $HBrO$ as titrand D, and NaOH solution as titrant T.

Keywords

Electrolytic redox systems; Oxidation numbers; GATES/GEB

Introduction

The Generalized Approach to Electrolytic Systems (GATES) [1-13] is the best thermodynamic approach to equilibrium and metastable electrolytic systems of any degree of complexity, where all necessary, physicochemical knowledge on the systems tested can be involved. The GATES is applicable, among others, (a) to mathematical modelling of redox and non-redox electrolytic systems, (b) in choice of optimal *a priori* conditions of chemical analyses, and (c) in

gaining the chemical information invisible in real experiments. The modelling of redox systems is based on general laws of elements and charge preservation, related to closed electrolytic systems composed of condensed (liquid or liquid+solid) phases, separated from the environment by diathermal walls.

The terms: components and species are distinguished. The species in aqueous systems are considered in their natural form, i.e. as hydrates $X_1^{z_1} \cdot n_{1W}$, where z_1 ($z_1 = 0, \pm 1, \pm 2, \dots$) is the charge of $X_1^{z_1}$, expressed in elementary charge unit $e = F/N_A$ (F – Faraday constant, N_A – Avogadro's constant), and n_{1W} (≥ 0) is the mean number of water ($W = H_2O$) molecules attached to $X_1^{z_1}$. The known chemical formulas of the $X_1^{z_1}$ and their respective external charges provide the information necessary/sufficient to formulate the respective balances [3], for elements or cores. A core is a cluster of elements with defined composition, expressed by its chemical formula, structure and external charge, that remains unchanged in a system considered, realized during the titration.

The titration is a dynamic procedure, where V mL of titrant T, containing a reagent B (C mol/L), is added into V_0 mL of titrand D, containing a substance A (C_0 mol/L). An advance of the titration $B(C, V) \Rightarrow A(C_0, V_0)$, denoted briefly as $B \Rightarrow A$, is characterized by the fraction titrated

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \quad (1)$$

That introduces a kind of normalization (independence on V_0 value) for titration curves, expressed by $pH = pH(\Phi)$, and $E = E(\Phi)$ for potential E [V] expressed in SHE scale. 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. The redox systems are modeled according to GATES/GEB principles.

In the notation applied here, N_{0j} ($j=1,2,\dots,J$) is the number of molecules of the component of j -th kind, including water, forming a static or dynamic D+T system, from titrand D and titrant T composed separately. The D+T system thus obtained involves N_1 molecules of H_2O and N_i species of i -th kind, $X_1^{z_1} \cdot n_{1W}$ ($i=2,3,\dots,I$), denoted briefly as $X_1^{z_1} \cdot (N_1, n_{1W})$, where $n_1 \equiv n_{1W} \equiv n_1 H_2O$. Molar concentration of the species $X_1^{z_1} \cdot n_{1W}$ is denoted as $[X_1^{z_1}]$. Except the $pH = pH(\Phi)$, and $E = E(\Phi)$ relationships, the D+T systems are represented graphically by speciation curves $\log [X_1^{z_1}] = \varphi_i(\Phi)$.

We consider here two systems with bromine as one electron-active disproportionating element [4,6,10]. 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 ($-1, -1/3, 0, 1, 5$), (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, (Figure 1).

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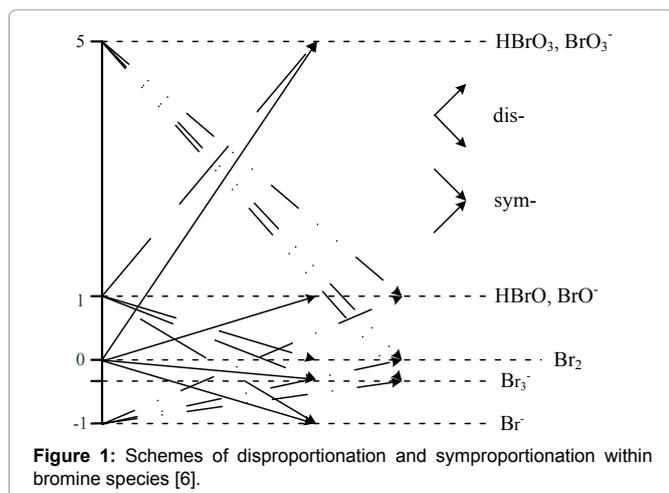
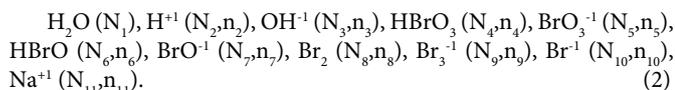


Figure 1: Schemes of disproportionation and symproportionation within bromine species [6].

We consider first two D+T systems: (S1) $\text{NaOH} \rightarrow \text{Br}_2$ and (S2) $\text{NaOH} \rightarrow \text{HBrO}$. In the system S1, V_0 mL of D is composed of Br_2 (N_{01} molecules) + H_2O (N_{02} molecules), and V mL of T is composed of NaOH (N_{03} molecules) + H_2O (N_{04} molecules). In the system S2, V_0 mL of D is composed of HBrO (N_{01} molecules) + H_2O (N_{02} molecules), and V mL of T is composed of NaOH (N_{03} molecules) + H_2O (N_{04} molecules).

In both systems (S1, S2), the D+T mixture involves the following species:



Let us assume that V mL of the titrant T is added into V_0 mL of the titrand D, up to a given point of the titration, and $V_0 + V$ mL of D+T mixture is obtained. Molar concentration (C_0) of the solute X in D (i.e. $X = \text{Br}_2$ or HBrO) is involved in relation

$$C_0 \cdot V_0 = 10^3 \cdot N_{01} / N_A \quad (3)$$

and molar concentration (C) of the solute $Y = \text{NaOH}$ in T is involved in relation

$$C \cdot V = 10^3 \cdot N_{03} / N_A \quad (4)$$

Molar concentrations $[X_i^{Z_i}]$ of the species in the D+T mixture are involved in the relations

$$[X_i^{Z_i}] \cdot (V_0 + V) = 10^3 \cdot N_i / N_A \quad (i=2, \dots, 11) \quad (5)$$

At $V=0$, the related system is limited to D, i.e. (S1) Br_2 (C_0) solution, or (S2) HBrO (C_0) solution, and we have

$$[X_i^{Z_i}] \cdot V_0 = 10^3 \cdot N_i / N_A \quad (i=2, \dots, 10) \quad (6)$$

In this paper, the redox systems will be formulated first according to the Approach II to GEB. Some problems involved with these systems will be discussed in details, and then generalized on more complex systems.

Formulation of the redox systems

The system S1

V_0 mL of D is composed of Br_2 (N_{01} molecules) + H_2O (N_{02} molecules), and V mL of T is composed of NaOH (N_{03} molecules) + H_2O (N_{04} molecules). The balances related to the D+T mixture are as follows:

$$f_0 = \text{ChB}$$

$$N_2 - N_3 - N_5 - N_7 - N_9 - N_{10} + N_{11} = 0 \quad (7)$$

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

$$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(1+2n_6) + 2N_7n_7 + 2N_8n_8 + 2N_9n_9 + 2N_{10}n_{10} + 2N_{11}n_{11} = 2N_{02} + N_{03} + 2N_{04} \quad (8)$$

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

$$N_1 + N_2n_2 + N_3(1+n_3) + N_4(3+n_4) + N_5(3+n_5) + N_6(1+n_6) + N_7(1+n_7) + N_8n_8 + N_9n_9 + N_{10}n_{10} + N_{11}n_{11} = N_{02} + N_{03} + N_{04} \quad (9)$$

$$f_3 = f(\text{Br})$$

$$N_4 + N_5 + N_6 + N_7 + 2N_8 + 3N_9 + N_{10} = 2N_{01} \quad (10)$$

$$-f_4 = -f(\text{Na})$$

$$N_{03} = N_{11} \quad (11)$$

Note, for example, that N_4 molecules ($z_4=0$) of $\text{HBrO}_3 \cdot n_4 \text{H}_2\text{O}$ involve: $N_4(1+2n_4)$ atoms of H, $N_4(3+n_4)$ atoms of O, and N_4 atoms of Br. From Equations 8 and 9 we have

$$f_{12} = 2f_2 - f_1: \quad -N_2 + N_3 + 5N_4 + 6N_5 + N_6 + 2N_7 = N_{03} \quad (12)$$

From Equations 7, 11 and 12

$$f_{12} + f_0 - f_4: \quad 5N_4 + 5N_5 + N_6 + N_7 - N_9 - N_{10} = 0 \quad (13)$$

Applying the atomic number $Z_{\text{Br}} (= 35)$ for Br, from Equations 10 and 13 we have

$$Z_{\text{Br}} f_3 - (f_{12} + f_0 - f_4): (Z_{\text{Br}} - 5)(N_4 + N_5) + (Z_{\text{Br}} - 1)(N_6 + N_7) + 2Z_{\text{Br}} N_8 + (3Z_{\text{Br}} + 1)N_9 + (Z_{\text{Br}} + 1)N_{10} = 2Z_{\text{Br}} N_{01} \quad (14)$$

Note, for example, that $f_4 = f(\text{Na}) \leftrightarrow f(\text{Na}) = f_4 \leftrightarrow -f_4 = -f(\text{Na})$.

The system S2

In the system S2, the set (2) of the species is identical as in the system S1. Applying similar notation, we assume that V_0 mL of D is composed of HBrO (N_{01} molecules) + H_2O (N_{02} molecules), and V mL of T is composed of NaOH (N_{03} molecules) + H_2O (N_{04} molecules). The $f_0 = \text{ChB}$ in the system S2 is identical with Equation 7, and $-f_4 = -f(\text{Na})$ is as in Equation 11. Then after formulation of the balances for the related D+T mixture:

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

$$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(1+2n_6) + 2N_7n_7 + 2N_8n_8 + 2N_9n_9 + 2N_{10}n_{10} + 2N_{11}n_{11} = N_{01} + 2N_{02} + N_{03} + 2N_{04} \quad (15)$$

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

$$N_1 + N_2n_2 + N_3(1+n_3) + N_4(3+n_4) + N_5(3+n_5) + N_6(1+n_6) + N_7(1+n_7) + N_8n_8 + N_9n_9 + N_{10}n_{10} + N_{11}n_{11} = N_{01} + N_{02} + N_{03} + N_{04} \quad (16)$$

$$f_3 = f(\text{Br}): \quad N_4 + N_5 + N_6 + N_7 + 2N_8 + 3N_9 + N_{10} = N_{01} \quad (17)$$

we have here, by turns,

$$f_{12} = 2f_2 - f_1: \quad -N_2 + N_3 + 5N_4 + 6N_5 + N_6 + 2N_7 = N_{01} + N_{03} \quad (18)$$

$$f_{12} + f_0 - f_4: \quad 5N_4 + 5N_5 + N_6 + N_7 - N_9 - N_{10} = N_{01} \quad (19)$$

$$Z_{Br} \cdot f_3 - (f_{12} + f_0 - f_4) : (Z_{Br}-5)(N_1+N_5) + (Z_{Br}-1)(N_6+N_7) + 2Z_{Br} \cdot N_8 + (3Z_{Br}+1)N_9 + (Z_{Br}+1)N_{10} = (Z_{Br}-1)N_{01} \quad (20)$$

In principle, the numbers N_{01} and N_{02} of the molecules composing the system S2 and the numbers N_i of the species in the related D+T mixture are different than that in the system S1.

Components versus species

Br_2 and H_2O forming D, and NaOH and H_2O forming T, are components of the system S1; HBrO and H_2O forming D, and NaOH and H_2O forming T, are components of the system S2. The species in (2) are present in the D+T systems (S1 and S2) thus formed. All components are uncharged entities, whereas the species are formed by charged (cations, anions) or uncharged (molecules) entities.

The systems S1 and S2 in terms of molar concentrations

For the systems S1 and S2, from Equations 5 and 7 we have

$$[H^+] - [OH^-] - [BrO_3^-] - [BrO^-] - [Br_3^-] - [Br^-] + [Na^+] = 0 \quad (7a)$$

For the system S1, from Equations 3–5, 10, 11 and 13, we have:

$$([HBrO_3] + [BrO_3^-]) + ([HBrO] + [BrO^-]) + 2[Br_2] + 3[Br_3^-] + [Br^-] = 2 \cdot C_0 V_0 / (V_0 + V) \quad (10a)$$

$$[Na^+] = CV / (V_0 + V) \quad (11a)$$

$$5([HBrO_3] + [BrO_3^-]) + ([HBrO] + [BrO^-]) - [Br_3^-] - [Br^-] = 0 \quad (13a)$$

Equations 10a and 11a are termed as concentration balances, obtained from elemental balances 10 and 11, and Equation 13a is the shorter form of GEB, expressed in terms of concentrations. The relation 11a can be immediately introduced into Equation 7a; then we get

$$[H^+] - [OH^-] - [BrO_3^-] - [BrO^-] - [Br_3^-] - [Br^-] + CV / (V_0 + V) = 0 \quad (7b)$$

Equations 7b, 10a and 13a form the complete set of balances related to the system S1.

For the system S2, from Equations 3–5, 17 and 19, we obtain the balances:

$$([HBrO_3] + [BrO_3^-]) + ([HBrO] + [BrO^-]) + 2[Br_2] + 3[Br_3^-] + [Br^-] = C_0 V_0 / (V_0 + V) \quad (17a)$$

$$5([HBrO_3] + [BrO_3^-]) + ([HBrO] + [BrO^-]) - [Br_3^-] - [Br^-] = C_0 V_0 / (V_0 + V) \quad (19a)$$

completed by the balance 7b.

We can also refer to static systems, formed by C_0 mol/L solutions of: (S1) Br_2 , (S2) HBrO. These solutions are identical with the titrand D in the related systems S1 and S2. The balances for the static systems are obtained assuming $V=0$ in Equations 7b and 10a for S1, or in Equations 7b, 17a and 19a for S2. Equation 13a is identical for the dynamic and static systems with C_0 mol/L Br_2 in D; Equation 7b is identical in S1 and S2.

Some Detailed Remarks

The remarks related to water molecules

The numbers: N_i , n_i ($i=2, \dots, I$), and N_{01} related to $W=H_2O$ molecules (i.e., free W as the species, W in hydrated species, and W as components) are cancelled within f_{12} . In other words, $I-1$ kinds of the species $X_1^{Z_1 \cdot n_{iW}}$ are involved in equations related to the system.

All $n_i = n_{iW}$ values are virtually unknown – even for $X_2^{Z_2} = H^+$ [14] in aqueous media, and depend on ionic strength (I) of the solution. The species $X_1^{Z_1 \cdot n_{iW}}$ with different n_{iW} values are considered equivalently. Also the $X_1^{Z_1}$'s with different numbers of H_2O molecules involved, e.g. $H_4IO_6^-$, IO_4^- ; $H_2BO_3^-$, $B(OH)_4^-$; AlO_2^- , $Al(OH)_4^-$ are considered equivalently, i.e., as the same species in this medium [11].

The Approach I to GEB

In C_0 mol/L Br_2 solution (D in the system S1), 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 $2Z_{Br}$ bromine electrons, i.e., N_{01} molecules of Br_2 involve $2Z_{Br} \cdot N_{01}$ bromine electrons. The oxidation degree x of an atom in a 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. We have, by turns, the relations: $1 \cdot 1 + 1 \cdot x + 3 \cdot (-2) = 0 \rightarrow x = 5$ for $HBrO_3$; $1 \cdot x + 3 \cdot (-2) = -1 \rightarrow x = 5$ for BrO_3^- ; $1 \cdot 1 + 1 \cdot x + 1 \cdot (-2) = 0 \rightarrow x = 1$ for HBrO; ... ; $3 \cdot x = -1 \rightarrow x = -1/3$; $1 \cdot x = -1 \rightarrow x = -1$ for Br^- .

The oxidation degree 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 HBrO₃ is calculated from the formula: $Z_{Br} \cdot (+1) + y \cdot (-1) = 5$, i.e., bromine involves $y = Z_{Br} - 5$ bromine electrons, etc. On this basis, we state that [10]:

N_4 species $HBrO_3 \cdot n_4 H_2O$ involve $(Z_{Br} - 5) \cdot N_4$ bromine electrons;

N_5 species $BrO_3^- \cdot n_5 H_2O$ involve $(Z_{Br} - 5) \cdot N_5$ bromine electrons;

N_6 species $HBrO \cdot n_6 H_2O$ involve $(Z_{Br} - 1) \cdot N_6$ bromine electrons;

N_7 species $BrO^- \cdot n_7 H_2O$ involve $(Z_{Br} - 1) \cdot N_7$ bromine electrons;

N_8 species $Br_2 \cdot n_8 H_2O$ involve $2Z_{Br} \cdot N_8$ bromine electrons;

N_9 species $Br_3^- \cdot n_9 H_2O$ involve $(3Z_{Br} + 1) \cdot N_9$ bromine electrons;

N_{10} species $Br^- \cdot n_{10} H_2O$ involve $(Z_{Br} + 1) \cdot N_{10}$ bromine electrons;

N_{01} molecules of Br_2 involved $2Z_{Br} \cdot N_{01}$ bromine electrons.

Equivalence of the Approaches I and II to GEB

Balancing of bromine electrons gives here Equation 14 (system S1), and then

$$(Z_{Br} - 5)([HBrO_3] + [BrO_3^-]) + (Z_{Br} - 1)([HBrO] + [BrO^-]) + 2Z_{Br}[Br_2] + (3Z_{Br} + 1)[Br_3^-] + (Z_{Br} + 1)[Br^-] = 2Z_{Br} C_0 V_0 / (V_0 + V) \quad (14a)$$

In the system S2, N_{01} molecules of HBrO brings $(Z_{Br} - 1) \cdot N_{01}$ bromine electrons, and from the related balancing we obtain Equation 20, and then

$$(Z_{Br} - 5)([HBrO_3] + [BrO_3^-]) + (Z_{Br} - 1)([HBrO] + [BrO^-]) + 2Z_{Br}[Br_2] + (3Z_{Br} + 1)[Br_3^-] + (Z_{Br} + 1)[Br^-] = (Z_{Br} - 1) C_0 V_0 / (V_0 + V) \quad (20a)$$

The equations: $14 \rightarrow 14a$ and $20 \rightarrow 20a$ are examples of formulation of GEB according to Approach I to GEB. The GEB formulation presented in the previous section 5.2, and considered as the Approach I to GEB in the related systems (S1 and S2), gives the Equations 14a

and 20a equivalent with equations 14 and 20; this means that the interdependence

$$\text{Approach I to GEB} \Leftrightarrow \text{Approach II to GEB} \quad (21)$$

is true [10].

Other equivalent forms of GEB

The f_{12} (Equation 18) and other combinations of f_{12} with f_0, f_3 and f_4 (Equations 7, 17, 11) have full properties of GEB for the system S1. Note that the GEB obtained for the system S2 from f_{12} (Equation 12) has the form

$$- [H^+] + [OH^-] + 5[HBrO_3] + 6[BrO_3^{-1}] + [HBrO] + 2[BrO^{-1}] = CV/(V_0+V) \quad (12a)$$

The GEB obtained for the system S2 from f_{12} (Equation 18) has the form

$$- [H^+] + [OH^-] + 5[HBrO_3] + 6[BrO_3^{-1}] + [HBrO] + 2[BrO^{-1}] = C_0V_0/(V_0+V) + CV/(V_0+V) \quad (18a)$$

One can also state that f_{12} (Equation 12) and other combinations of the f_{12} with f_0, f_3 and f_4 (Equations 7, 10, 11) have full properties of GEB for the system S1. For example, we have:

$$(f_{12} + f_0 + f_3 - f_4)/2 : 3(N_4 + N_5) + N_6 + N_7 + N_8 + N_9 = N_{01} \rightarrow (22)$$

$$3([HBrO_3] + [BrO_3^{-1}]) + [HBrO] + [BrO^{-1}] + [Br_2] + [Br_3^{-1}] = C_0V_0/(V_0+V) \quad (22a)$$

For the system S2, the relations derived for $(f_{12} + f_0 + f_3 - f_4)/2$ are identical with equations 22 and 22a.

Minimal number of constituents as a criterion of GEB simplicity

As were stated above, $f_{12}, f_{12}+f_0$ and any linear combination of f_{12} with f_0, f_3, \dots, f_i related to the system in question, i.e.,

$$f = f_{12} + a_0 \cdot f_0 + \sum_{k=3}^K a_k \cdot f_k \quad (\text{where } a_k \in R \text{ for } k=0,3,4,\dots,K) \quad (23)$$

Have full properties of GEB. An interesting matter is here the selection of such a_k coefficients where the linear combination contains the minimal number of constituents (species, components), after all cancellations done in (23). We calculate the summary number $S_m = I_m + J_m$ of constituents in Equation (23), where I_m – the number of species, and J_m – the number of components. We refer here to the systems S1 and S2.

For the system S1 we have: $S_{m1} = 6+0 = 6$ from (13a), $S_{m2} = 7+1 = 8$ from (14a), $S_{m3} = 6+1 = 7$ from (12a), $S_{m4} = 6+1 = 7$ from (22a). For the system S2 we have: $S_{m1} = 6+1 = 7$ from (19a), $S_{m2} = 7+1 = 8$ from (20a), $S_{m3} = 6+2 = 8$ from (18a), $S_{m4} = 6+1 = 7$ from (22a). Then we have minimal $(S_m)_{\min} = 6$ for the system S1, and $(S_m)_{\min} = 6$ for the system S2. The linear combinations with smaller number S_m are not obtainable for the systems S1 and S2 and then $(S_m)_{\min} > 0$ in both instances, i.e., the combination (23) is not transformed there to identity $0 = 0$. Note that I_m 's in (12a) and (18a) involve 2 components related to the species ($H^{+1} \cdot n_{2W}$, $OH^{-1} \cdot n_{3W}$) and 1 compound (NaOH), related to the entities composed only of 'fans': H, O, Na.

Electron-active and electron-non-active elements

In the systems S1 and S2, we have only one electron-active element: bromine (Br), as (S1) Br_2 or (S2) $HBrO$, i.e. as the components on the intermediary oxidation states: 0 in (S1), and +1 in

(S2), able to disproportionation in aqueous media, see Figure 1. The Br_2 in S1 or $HBrO$ in S2 are characterized as 'distributors' of electrons in the related systems. Note that Br_2 and $HBrO$ do not oxidize water molecules, i.e., products of H_2O oxidation do not exist (are not formed) there as species. Hydrogen (H), oxygen (O) and sodium (Na) are electron-non-active elements in the systems S1 and S2.

In all instances, the (partial) linear combination $f_{12}+f_0$ is applied for cancellation purpose; $-N_2+N_3 = -(N_2-N_3)$ are cancelled within the sum $f_{12}+f_0$ related to redox and non-redox systems.

Oxidation number, oxidant and reductant as the redundant terms

The GEB related to the system S1 with Br_2 (C_0) and expressed by Equation 13a, obtained according to Approach II to GEB, can be rewritten as follows:

$$1 \cdot (+5) \cdot ([HBrO_3] + [BrO_3^{-1}]) + 1 \cdot (+1) \cdot ([HBrO] + [BrO^{-1}]) + 2 \cdot 0 \cdot [Br_2] + 3 \cdot (-1/3) \cdot [Br_3^{-1}] + 1 \cdot (-1) \cdot [Br^{\cdot-}] = 2 \cdot (0) \cdot C_0V_0/(V_0+V) \quad (13b)$$

Whereas the GEB related to the system S2 with $HBrO$ (C_0) and expressed by Equation 19a, obtained according to Approach II to GEB, can be rewritten as follows:

$$1 \cdot (+5) \cdot ([HBrO_3] + [BrO_3^{-1}]) + 1 \cdot (+1) \cdot ([HBrO] + [BrO^{-1}]) + 2 \cdot 0 \cdot [Br_2] + 3 \cdot (-1/3) \cdot [Br_3^{-1}] + 1 \cdot (-1) \cdot [Br^{\cdot-}] = 1 \cdot (+1) \cdot C_0V_0/(V_0+V) \quad (19b)$$

As we see, in the balances obtained from $f_{12}+f_0$, the oxidation numbers in particular Br-species are equal to (or involved with) the coefficient/multiplier at the concentration of the corresponding species with electron-active element (here: Br), and in the component (Br_2 or $HBrO$) or bromine species. If the species or component involves more atoms of an electron-active element, then the coefficient is equal to the product of the related numbers; e.g. $-[Br_3^{-1}] = (-1)[Br_3^{-1}] = 3 \cdot (-1/3) \cdot [Br_3^{-1}]$ in Equation 13a or 19a, where 3 = number of Br-atoms, $-1/3$ = oxidation number of Br in Br_3^{-1} .

Concluding,

(1) the formulation of GEB according to Approach II to GEB, i.e., where f_{12} is calculated, needs none prior knowledge of the oxidation states (oxidation numbers) of all elements participating the system S1 or S2, i.e., Br, H, O; it means that the oxidation state (oxidation number) is the derivative concept within GATES/GEB;

(2) the terms: oxidant and reductant are not distinguished, i.e., not ascribed *a priori* to particular components and species in electrolytic systems, considered according to GATES/GEB principles, with GEB obtained according to Approaches I and II to GEB; full 'democracy' in this respect is assumed.

Comparison of the Approaches I and II to GEB

The Approach I to GEB [10], named as the 'short' version of GEB, needs the knowledge of oxidation numbers for all elements in all the species participating the system considered. This knowledge is not required in the Approach II to GEB; the known composition (chemical formula) of a species and its external charge are quite sufficient for this purpose. This property of the Approach II to GEB is of capital importance, particularly in context with complex organic substances/compounds and species involved in redox equilibria. Thus, the Approach II to GEB offers very essential advantages, when

compared with the Approach I to GEB. The regularities involved with water molecules are valid for both (I and II) Approaches to GEB.

Equations and equalities

Among the concentration balances one can distinguish equations and equalities. An equality, represented by the balance (11a), involves only one species (here: Na^+), whereas an equation for concentration balance involves more species, see Equations 10a or 17a. In the equality (11a), the value for $[\text{Na}^+]$ is a number for the pre-assumed C and V_0 values, at given V-value; as such, it can enter immediately the related ChB, see Equation 7b. Then (11a) is not considered as equation, when the number of equations be compared with the number of independent variables.

Number of independent equations and dependency/independency property

In the system S1, three equations: {7b, 10a, 13a} form a set of three independent equations. In this context, four equations: {7b, 10a, 13a, 14a} or {7a, 10a, 13a, 22a}, and the more the five equations: {7a, 10a, 13a, 14a, 22a} form a set of linearly dependent equations in the System S1; in other words, the set of equations: {7a, 10a, 13a} or {7a, 10a, 14a} or {7a, 10a, 22a} can be chosen, optionally, as the set of equations involved in the algorithm applied for calculation purposes, see computer program in section 3.14, where Eq. 14a is involved.

Completeness of equilibrium constants

The first step in the formulation of redox systems according to GATES/GEB principles is gathering of the corresponding equilibrium data, i.e., the standard potentials E_{0p} , and other equilibrium constants [1]. The set of equilibrium constants should be complete, as far as possible. The point is that these sets of data, often presented in the corresponding tables of equilibrium constants, are usually incomplete and/or refer to different equations of the related reactions. The related equilibrium constants can be obtained from other equilibrium constants, as will be shown below. Often, the tables of equilibrium constants contained in some studies are characterized by redundancy, i.e., the seemingly excessive number of physicochemical data, collected from various thematic studies, from different source works. Equilibrium constants values are subjected to errors – which means that even the results of tests performed under identical conditions may differ, in principle. The equilibrium constants are determined experimentally, by appropriate physicochemical methods. These equilibrium constants are parameters in the appropriate mathematical models, resolved with use of computer programs.

Relations between concentrations of the species; number of independent variables

From the interrelations obtained on the basis of complete set of independent expressions for equilibrium data chosen from ones collected in Table 1 (column D) [15], we have [8,10]:

$$[\text{H}^+] = 10^{\text{pH}}; [\text{OH}^-] = 10^{\text{pH}-14}; [\text{BrO}_3^-] = 10^{6A(E-1.45)-\text{pBr}+6\text{pH}}; [\text{BrO}^-] = 10^{2A(E-0.76)-\text{pBr}+2\text{pH}-28};$$

$$[\text{Br}_2] = 10^{2A(E-1.087)-2\text{pBr}}; [\text{Br}_3^-] = 10^{2A(E-1.05)-2\text{pBr}}; [\text{HBrO}_3] = 10^{0.7-\text{pH}}; [\text{BrO}_3^-]; [\text{HBrO}] = 10^{8.6-\text{pH}}; [\text{BrO}^-] \quad (24)$$

where the uniformly defined, three scalar variables: E, pH and pBr, forming a vector $\mathbf{x} = (x(1), x(2), x(3)) = (E, \text{pH}, \text{pBr})^T$, are involved, where:

$$A \cdot E = -\log[e^-], \text{pH} = -\log[\text{H}^+], \text{pBr} = -\log[\text{Br}^-] \quad (25)$$

Three independent variables: $\mathbf{x}^T = (E, \text{pH}, \text{pBr})$ are involved in the systems S1 and S2 where, informally, E is ascribed to GEB (Equations 13a, 14a, or 22a), pH to ChB (Equation 7b), and pBr to the concentration balance for Br (Equation 10a).

The interrelations (24) were obtained on the basis of selected values for the corresponding, independent equilibrium constants presented in Table 1. All the variables in (24) are in the exponents of the power for 10 in: $[e^-] = 10^{-A \cdot E}$, $[\text{H}^+] = 10^{-\text{pH}}$, $[\text{Br}^-] = 10^{-\text{pBr}}$, where $1/A = RT/F \cdot \ln 10$; $A = 16.9$ at $T = 298$ K. The number of the (independent, 'homogeneous') variables equals to the number of equations, $3 = 3$; this ensures a unique solution of the equations related to the systems S1 and S2, at the preset C_0 , C and V_0 values, and the V-value at which the calculations are realized, at defined step of the calculation procedure, according to iterative computer program presented in section 5.14. The E_{0j} values were taken from references [15-18].

In Table 1 (numbers 5,10,15) we have also the data involved with liquid bromine, $\text{Br}_{2(0)}$. Solubility of $\text{Br}_{2(0)}$ is 35 g/L (20 °C) [19], i.e. $s = 0.22 \text{ mol/L} > C_0 = 10^{-2} \text{ mol/L}$, and then $[\text{Br}_{2(0)}] = 0$ in the systems S1, S2. HBrO_4 is considered as unstable species [20,21].

Compatibility of the equilibrium constants

On the basis of $E_{02B} = 1.482$ V (Table 1) and K_W , we can calculate K_{e6} and E_{06} for reaction $\text{BrO}_3^- + 3\text{H}_2\text{O} + 5e^- = \frac{1}{2} \text{Br}_2 + 6\text{OH}^-$. From K_{e2} and $[\text{Br}^-]^{0.5}[\text{OH}^-]^6 = K_{e6}[\text{BrO}_3^-][e^-]^5$ we have, by turns: $K_{e6} = K_{e2}(K_W)^6 \rightarrow \log K_{e6} = \log K_{e2} - 6\text{p}K_W \rightarrow 5AE_{06} = 5AE_{02B} - 6\text{p}K_W$; the value $E_{06} = 1.482 - 6 \cdot 14 / (5 \cdot 16.9) = 0.4879 \neq E_{06D} = 0.50$ V in Table 1.

On the basis of $E_{017} = 0.68$ V for $\text{BrO}_4^-/\text{Br}^-$ pair at $\text{pH} = 14$ [22] and K_W , we calculate K_e and then E_0 for $\text{BrO}_4^- + 8\text{H}^+ + 8e^- = \text{Br}^- + 4\text{H}_2\text{O}$. For $\text{BrO}_4^- + 4\text{H}_2\text{O} + 8e^- = \text{Br}^- + 8\text{OH}^-$ we have $[\text{Br}^-][\text{OH}^-]^8 = K_{e17}[\text{BrO}_4^-][e^-]^8$; then $K_e = K_{e17}/(K_W)^8 \rightarrow \log K_e = \log K_{e17} + 8\text{p}K_W \rightarrow 8AE_0 = 8AE_{017} + 8\text{p}K_W \rightarrow E_0 = 0.68 + 14/16.9 = 1.5084$ V.

On the basis of E_{01A} and E_{07B} (Table 1) we calculate K_e and E_0 for the reaction $\text{BrO}_4^- + 8\text{H}^+ + 8e^- = \text{Br}^- + 4\text{H}_2\text{O}$ we get $E_0 = 0.25 \cdot 1.745 + 0.75 \cdot 1.423 = 1.5035 \neq 1.5084$ V.

On the basis of Table 1 we obtain, by turns: $(K_{e7})^2/(K_{e5})^2 = K_{e14} \rightarrow 2\log K_{e7} - 2\log K_{e5} = \log K_{e14} \rightarrow 2\log K_{e7} = 2\log K_{e5} + \log K_{e14} \rightarrow 2 \cdot 6AE_{07} = 2 \cdot 5AE_{05A} + 2 \cdot AE_{014B} \rightarrow E_0 = E_{07} = (5E_{05A} + E_{014B})/6 = (5 \cdot 1.513 + 1.098)/6 = 1.4438 \text{ V} \neq E_{07B}, E_{07D}$.

In the links we do not find the $\text{p}K_{11}$ values for $\text{HBrO} = \text{H}^+ + \text{BrO}^-$, $K_{11} = [\text{H}^+][\text{BrO}^-]/[\text{HBrO}]$. However, we can find it on the basis of relations:

$$(a) \text{p}K_{11} = \log K_{e12} - \log K_{e11} + 2 \cdot \text{p}K_W; \text{ e.g. (a1) } \text{p}K_{11} = 2 \cdot 16.9 \cdot (E_{012B} - E_{011B}) + 2 \cdot 14 = 8.734; (a2) \text{p}K_{11} = 2 \cdot 16.9 \cdot (E_{012A} - E_{011B}) + 2 \cdot 14 = 8.903; (a3) \text{p}K_{11} = 2 \cdot 16.9 \cdot (E_{012D} - E_{011B}) + 2 \cdot 14 = 8.700;$$

(b) $\text{p}K_{11} = \log K_{e12} - 0.5 \cdot \log K_{e14} - \log K_{e9} + 2\text{p}K_W$; e.g., (b1) $\text{p}K_{11} = 16.9 \cdot (2 \cdot E_{012A} - E_{014A} - E_{09B}) + 2 \cdot 14 = 8.734$; (b2) $\text{p}K_{11} = 16.9 \cdot (2 \cdot E_{012B} - E_{014C} - E_{09B}) + 2 \cdot 14 = 8.751$; (b3) $\text{p}K_{11} = 16.9 \cdot (2 \cdot E_{012D} - E_{014B} - E_{09B}) + 2 \cdot 14 = 8.712$; etc. The K_{11} values calculated on the basis of E_{0k} values are not far distant from the $\text{p}K_{11}$ values: 8.6 and 8.7 cited elsewhere (Table 1).

In conclusion, the relevant data found that do not differ dramatically among themselves [15-18].

It should be added that the data in columns A,B in Table 1 refer only to E_{0k} . In addition, these equilibrium constants do not relate to

Table 1: Equilibrium data related to different bromine species taken from the references indicated in columns A-D; the standard potentials (E_0) values are expressed in SHE scale.

No	Reaction	Equilibrium relation	A [16]	B [17]	C [18]	D [15]
1	$\text{BrO}_4^{-1} + 2\text{H}^{+1} + 2\text{e}^{-1} = \text{BrO}_3^{-1} + \text{H}_2\text{O}$	$[\text{BrO}_3^{-1}] = K_{e1} [\text{BrO}_4^{-1}] [\text{H}^{+1}]^2 [\text{e}^{-1}]^2$	$E_{01A} = 1.745$			
2	$\text{BrO}_3^{-1} + 6\text{H}^{+1} + 5\text{e}^{-1} = \frac{1}{2} \text{Br}_2 + 3\text{H}_2\text{O}$	$[\text{Br}_2]^{0.5} = K_{e2} [\text{BrO}_3^{-1}] [\text{H}^{+1}]^6 [\text{e}^{-1}]^5$		$E_{02B} = 1.482$		$E_{02D} = 1.52$
3	$\text{BrO}_3^{-1} + 5\text{H}^{+1} + 4\text{e}^{-1} = \text{HBrO} + 2\text{H}_2\text{O}$	$[\text{BrO}^{-1}] [\text{OH}^{-1}]^4 = K_{e4} [\text{BrO}_3^{-1}] [\text{e}^{-1}]^4$				$E_{03D} = 1.45$
4	$\text{BrO}_3^{-1} + 2\text{H}_2\text{O} + 4\text{e}^{-1} = \text{BrO}^{-1} + 4\text{OH}^{-1}$	$[\text{BrO}^{-1}] [\text{OH}^{-1}]^4 = K_{e4} [\text{BrO}_3^{-1}] [\text{e}^{-1}]^4$			$E_{04C} = 0.54$	$E_{04D} = 0.54$
5	$\text{BrO}_3^{-1} + 6\text{H}^{+1} + 5\text{e}^{-1} = \frac{1}{2} \text{Br}_{2(l)} + 3\text{H}_2\text{O}$	$[\text{Br}_{2(l)}]^{0.5} = K_{e5} [\text{BrO}_3^{-1}] [\text{H}^{+1}]^6 [\text{e}^{-1}]^5$	$E_{05A} = 1.513$			
6	$\text{BrO}_3^{-1} + 3\text{H}_2\text{O} + 5\text{e}^{-1} = \frac{1}{2} \text{Br}_2 + 6\text{OH}^{-1}$	$[\text{Br}_2]^{0.5} [\text{OH}^{-1}]^6 = K_{e6} [\text{BrO}_3^{-1}] [\text{e}^{-1}]^5$				$E_{06D} = 0.50$
7	$\text{BrO}_3^{-1} + 6\text{H}^{+1} + 6\text{e}^{-1} = \text{Br}^{-1} + 3\text{H}_2\text{O}$	$[\text{Br}^{-1}] = K_{e7} [\text{BrO}_3^{-1}] [\text{H}^{+1}]^6 [\text{e}^{-1}]^6$		$E_{07B} = 1.423$		$E_{07D} = 1.45$
8	$\text{BrO}_3^{-1} + 3\text{H}_2\text{O} + 6\text{e}^{-1} = \text{Br}^{-1} + 6\text{OH}^{-1}$	$[\text{Br}^{-1}] [\text{OH}^{-1}]^6 = K_{e8} [\text{BrO}_3^{-1}] [\text{e}^{-1}]^6$	$E_{08A} = 0.613$	$E_{08B} = 0.61$	$E_{08C} = 0.61$	$E_{08D} = 0.61$
9	$\text{HBrO} + \text{H}^{+1} + \text{e}^{-1} = \frac{1}{2} \text{Br}_2 + \text{H}_2\text{O}$	$[\text{Br}_2]^{0.5} = K_{e9} [\text{HBrO}] [\text{H}^{+1}] [\text{e}^{-1}]$		$E_{09B} = 1.574$		$E_{09D} = 1.6$
10	$\text{HBrO} + \text{H}^{+1} + \text{e}^{-1} = \frac{1}{2} \text{Br}_{2(l)} + \text{H}_2\text{O}$	$[\text{Br}_{2(l)}]^{0.5} = K_{e10} [\text{HBrO}] [\text{H}^{+1}] [\text{e}^{-1}]$	$E_{010A} = 1.584$	$E_{010B} = 1.596$		
11	$\text{HBrO} + \text{H}^{+1} + 2\text{e}^{-1} = \text{Br}^{-1} + \text{H}_2\text{O}$	$[\text{Br}^{-1}] = K_{e11} [\text{HBrO}] [\text{H}^{+1}] [\text{e}^{-1}]^2$		$E_{011B} = 1.331$		$E_{011D} = 1.34$
12	$\text{BrO}^{-1} + \text{H}_2\text{O} + 2\text{e}^{-1} = \text{Br}^{-1} + 2\text{OH}^{-1}$	$[\text{Br}^{-1}] [\text{OH}^{-1}]^2 = K_{e12} [\text{BrO}^{-1}] [\text{e}^{-1}]^2$	$E_{012A} = 0.766$	$E_{012B} = 0.761$		$E_{012D} = 0.76$
13	$2\text{BrO}^{-1} + 2\text{H}_2\text{O} + 2\text{e}^{-1} = \text{Br}_2 + 4\text{OH}^{-1}$	$[\text{Br}_2] [\text{OH}^{-1}]^4 = K_{e13} [\text{BrO}^{-1}]^2 [\text{e}^{-1}]^2$			$E_{013C} = 0.45$	$E_{013D} = 0.45$
14	$\text{Br}_2 + 2\text{e}^{-1} = 2\text{Br}^{-1}$	$[\text{Br}^{-1}]^2 = K_{e14} [\text{Br}_2] [\text{e}^{-1}]^2$	$E_{014A} = 1.098$	$E_{014B} = 1.0873$	$E_{014C} = 1.087$	$E_{014D} = 1.087$
15	$\text{Br}_{2(l)} + 2\text{e}^{-1} = 2\text{Br}^{-1}$	$[\text{Br}^{-1}]^2 = K_{e15} [\text{Br}_{2(l)}] [\text{e}^{-1}]^2$	$E_{015A} = 1.078$	$E_{015B} = 1.066$	$E_{015C} = 1.065$	
16	$\text{Br}_3^{-1} + 2\text{e}^{-1} = 3\text{Br}^{-1}$	$[\text{Br}^{-1}]^3 = K_{e16} [\text{Br}_3^{-1}] [\text{e}^{-1}]^2$	$E_{016A} = 1.062$		$E_{016C} = 1.05$	$E_{016D} = 1.05$
17	$\text{HBrO}_3 = \text{H}^{+1} + \text{BrO}_3^{-1}$	$[\text{H}^{+1}] [\text{BrO}_3^{-1}] = K_{11} [\text{HBrO}_3]$			$\text{p}K_{s1C} = 0.7$	
18	$\text{HBrO} = \text{H}^{+1} + \text{BrO}^{-1}$	$[\text{H}^{+1}] [\text{BrO}^{-1}] = K_{11} [\text{HBrO}]$			$\text{p}K_{11C} = 8.6$	$\text{p}K_{11D} = 8.7$
19	$\text{H}_2\text{O} = \text{H}^{+1} + \text{OH}^{-1}$	$[\text{H}^{+1}] [\text{OH}^{-1}] = K_W$			$\text{p}K_{WC} = 14.0$	$\text{p}K_{WD} = 14.0$

Note: $\log K_{ek} = n_k \cdot A \cdot E_{ok}$; $A = 16.9$; $\text{p}K_{s1} = -\log K_{s1}$, $\text{p}K_{11} = -\log K_{11}$, $\text{p}K_W = -\log K_W$

the same stoichiometric reactions. However, based on the E_{ok} values for the corresponding redox reactions one can obtain the values of other constants, e.g. concerning dissociation constants of the acid (here: HBrO).

A redundancy of the relevant data can also be noted – which means that some of the equilibrium constants from the given literature source can be obtained from other constants contained in that source. For example, from numbers 4, 6 and 13 in Table 1 we

get $K_{e13D} = (K_{e6D})^2 / (K_{e4D})^2 \rightarrow \log K_{e13D} = 2 \log K_{e6D} - \log K_{e4D} \rightarrow 2AE_{013D} = 2.5AE_{06D} - 2.4AE_{04D} \rightarrow E_{013D} = 5E_{06D} - 4E_{04D} = 5 \cdot 0.5 - 4 \cdot 0.54 = 0.34 \neq 0.45$; the difference is greater, in this case. Note that E_{04D} , E_{06D} and E_{013D} were not involved in the set of relations (24) and in the computer program presented above.

Even a small mismatch error resulting, for example, from the rounding of numerical values of the corresponding data, may cause a contradiction of the appropriate equations, where such constants are included within the same algorithm. Therefore, of primary importance is the selection of equilibrium constants that are independent to each other [23].

Computer program for the NaOH → Br₂ system

```
function F = NaOH_Br2(x)
global V C0 V0 C yy

E = x(1);
pH = x(2);
pBr = x(3);

H = 10^(-pH);
Kw = 10^-14;
pKw = 14;
OH = Kw/H;
A = 16.9;
Br = 10^-pBr;
ZBr = 35;

Br2=Br^2*10^(2*A*(E-1.087));
Br3=Br^3*10^(2*A*(E-1.05));
BrO=Br*10^(2*A*(E-0.76)+2*pH-2*pKw);
BrO3=Br*10^(6*A*(E-1.45)+6*pH);
HBrO = 10^8.6*H*BrO;
HBrO3=10^0.7*H*BrO3;
Na=C*V/(V0+V);

F = [%Charge balance
(H-OH+Na-Br-Br3-BrO-BrO3);
%Concentration balance for Br
(Br+3*Br3+2*Br2+HBrO+BrO+HBrO3+BrO3-2*C0*V0/(V0+V));
%Electron balance
((ZBr+1)*Br+(3*ZBr+1)*Br3+2*ZBr*Br2+(ZBr-1)*(HBrO+BrO)...
+(ZBr-5)*(HBrO3+BrO3)-2*ZBr*C0*V0/(V0+V)];
```

```
yy(1)=log10(Br);
yy(2)=log10(Br3);
yy(3)=log10(Br2);
yy(4)=log10(HBrO);
yy(5)=log10(BrO);
yy(6)=log10(HBrO3);
yy(7)=log10(BrO3);
yy(8)=log10(Na);
end
```

The volume V of the titrant (T) added is considered as a parameter, not variable; the V value is changed, in steps, in the calculation procedure, realized according to iterative computer program, here: MATLAB [1].

Final Comments

Calculations and graphical presentation of results

The calculation procedure, realized according to an iterative computer program, e.g. MATLAB, gives the set of points (Φ, pH, E). The data thus obtained can be presented numerically or graphically. Some results obtained for the system S1 are presented in Table 1. The titration curves: E = E(Φ) and pH = pH(Φ) for the systems S1 and S2 are presented in Figure 2 together with speciation diagrams, where the curves $\log[x_i^{z_i}] = \varphi_i(\Phi)$ were plotted for different bromine species (Table 2).

Before 2006, the basic property of the balance $2f(O) - f(H)$ for redox systems was unknown at all in the scientific world, and the linear independency/dependency of $2f(O) - f(H)$ as the fundamental/practical criterion distinguishing redox/non-redox systems of any degree of complexity was also unknown. The principles of GEB formulation were unknown in earlier literature. Here is the hidden simplicity, which had to be discovered by Michalowski, as the Approach II to GEB. The discovery of the Approach II GEB would most likely be impossible without the prior discovery (1992) of the Approach I to GEB by Michalowski.

The generalized electron balance (GEB) concept, valid for redox electrolytic systems, is considered as the law of Nature [3,8,10] related to electrolytic redox systems. The computer software applied to redox systems, denoted as GATES/GEB, is the emanation of balances for H and O, referred to aqueous media. The GEB is compatible with other (charge and concentration) balances and enables to resolve the electrolytic (mono- or/and two-phase) redox systems of any degree of complexity, within the scope of generalized approach to electrolytic systems (GATES), perceived as the thermodynamic approach to equilibrium and metastable systems, where all necessary physicochemical knowledge on the systems tested is involved. The advantages of GATES are illustrated on examples of redox and non-redox analytical systems. The GATES is perceived as the unrivalled tool applicable, among others: (a) to mathematical modelling of thermodynamic behavior of the systems, (b) in choice of optimal *a priori* conditions of chemical analyses, and (c) in gaining chemical information invisible in real experiments, in general. Furthermore, GATES is the basis for generalized equivalence mass (GEM) concept [24], considered as the advantageous alternative against

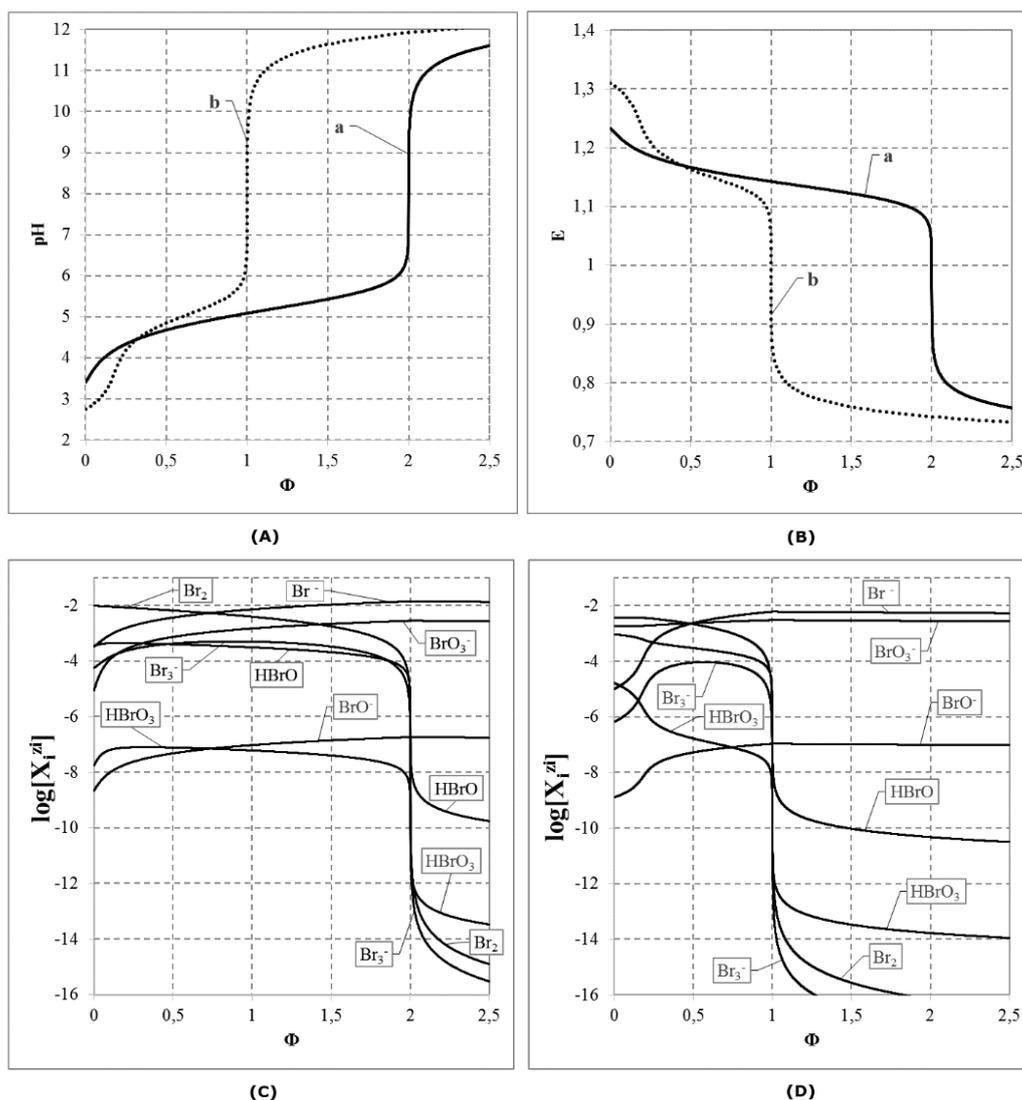


Figure 2: The relationships: (A) $\text{pH} = \text{pH}(\Phi)$ and (B) $E = E(\Phi)$ for the systems S1 and S2, and the related speciation diagrams for the systems: 1 (C) and 2 (D), at $V_0=100$, $C_0=0.01$, $C=0.1$. The curves a and b in Figures 2A and 2B are related to the systems S1 and S2, respectively.

the obligatory equivalence mass/“weight” concept, still suggested by IUPAC. According to GATES, any chemical reaction notation is only a basis to formulate the related expression for equilibrium constant according to mass action law.

GATES/GEB allows to track not only the individual titrations, but also the processes composed of several steps, as shown in the example of copper iodometric determination [9]; the entire analytical process is partitioned here into 4 stages: two preparatory stages, with non-redox reactions, and two further stages in which redox reactions occurred. The majority of the dynamic systems, realized according to titrimetric mode, is perceived also as an important tool in the classical chemical analysis.

The Approach II to GEB does not require any prior knowledge of the oxidation numbers of elements in the components and in the species; it is a fact of capital importance, particularly in relation to organic species (molecules, ions, radicals and ion-radicals), of any degree of complexity. Note that the ‘oxidation number’ was essentially

the contractual concept [25-27]. If the oxidation numbers are easily determined, the Approach I to GEB, known as the ‘short’ version of GEB, can be applied. Within the Approaches I and II to GEB, the roles/terms of oxidants and reductants are not assigned *a priori* to individual components; GATES/GEB provides full ‘democracy’ in this regard.

For all redox systems, any linear combination of $f_{12} = 2 \cdot f(\text{O}) - f(\text{H})$ with charge balance $f_0 = \text{ChB}$ and other elemental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) related to a redox system of any degree of complexity does not give the identity, $0 = 0$, see e.g. [23]. The f_{12} is linearly dependent on f_0, f_3, \dots, f_K when related to non-redox systems. In other words, the set of K independent balances $f_0, f_{12}, f_3, \dots, f_K$ is applied for a redox system, or a set of $K-1$ balances f_0, f_3, \dots, f_K is applied to a non-redox system with $K-2$ independent elemental/core balances $f_k = f(Y_k)$ for $Y_k \neq \text{H}, \text{O}$. The independency or dependency property of f_{12} is then the general criterion distinguishing between redox and non-redox systems [4,11,23] of any degree of complexity, also in mixed-

Table 2: The sets of (Φ , pH, E) values taken from the vicinity of the equivalence points for the systems S1 and S2, at $V_0=100$, $C_0=0.01$, $C=0.1$.

System S1			System S2		
NaOH \rightarrow Br ₂			NaOH \rightarrow HBrO		
Φ	pH	E	Φ	pH	E
1,995	6,666	1,0491	0,995	6,347	1,0720
1,996	6,728	1,0455	0,996	6,411	1,0681
1,997	6,811	1,0406	0,997	6,498	1,0630
1,998	6,933	1,0334	0,998	6,625	1,0555
1,999	7,161	1,0199	0,999	6,866	1,0412
2,000	8,143	0,9619	1,000	8,102	0,9682
2,001	8,966	0,9132	1,001	9,002	0,9150
2,002	9,244	0,8968	1,002	9,281	0,8985
2,003	9,413	0,8868	1,003	9,450	0,8885
2,004	9,534	0,8797	1,004	9,571	0,8814
2,005	9,628	0,8741	1,005	9,666	0,8758

solvent media [28-30].

The difference between redox and non-redox systems is then 'coded' in f_{12} . This unique, general property explains clearly why the elemental balances: f_1 and f_2 are not formulated for non-redox systems, of any degree of complexity. The f_{12} and any linear combination of f_{12} with f_0, f_3, \dots, f_k for a given system retain full properties of the GEB. In other words, f_{12} is fully compatible with other (f_0, f_3, \dots, f_k) balances and enables to resolve any electrolytic (mono- or/and two-phase) redox system within GATES, and GATES/GEB in particular.

All the inferences made within GATES/GEB are based on firmly established physical, physicochemical and algebraic foundations. Consequently, it allows to understand far better the 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 and preselected physicochemical knowledge involved.

Contrary to appearances, established by the current paradigm, the criterion distinguishing non-redox and redox systems is not immediately associated with free electrons in the related system; it provides a kind of uniformity in the formulas derived for this purpose. This fact, especially the simple calculations [9] of free electron concentrations in redox systems, deny the unique role of free electrons in elementary redox reactions, as described in half- or partial reactions, where the species of the same element with different oxidation numbers are involved. On the other hand, it points to the unique role of H and O in redox systems, suggested in earlier theoretical/hypothetical/qualitative considerations on these systems. Let's repeat: the GEB concept, valid for redox electrolytic systems, is the emanation of balances for H and O, referred to aqueous media.

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