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

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Abstract
The linear combination \( f_{\text{e}} = 2f(O) - f(H) \) of elemental balances: \( f_e = f(H) \) for H, and \( f_e = f(O) \) for O is the basis to formulate the generalized electrolytic approach (GATES) 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 \( (f_c = \text{CHB}) \) and K–2 elemental/core balances \( f_{\text{n}} \), the \( f_{\text{e}} \) 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 \( f_{\text{n}} \) with \( f_{\text{e}} \) and \( f_e = f(Y_k) \) \((Y_k \neq \text{H, O}; \ k=3, \ldots, \ K)\) gives the identity, \( 0 = 0 \). Consequently, in non-redox systems, \( f_{\text{e}} \) is linearly dependent on \( f_{\text{n}}, f_{\text{n}}^1, \ldots, f_{\text{n}}^i \), (.., \( f_{\text{n}}^i \)) is not the independent balance. This independency/dependency property of \( f_{\text{e}} \), distinguishes between redox and non-redox systems. In a redox system, a proper linear combination of \( f_{\text{n}} \) with \( f_{\text{e}} \) and 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) \( \text{Br}_2 \), and (S2) \( \text{HBrO} \) as titrand D, and \( \text{NaOH} \) 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 reducible and non-reducible 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 \( X_i^{Z_i} n_W \), where \( Z_i \) \((Z_i = 0, \pm 1, \pm 2, \ldots)\) is the charge of \( X_i^{Z_i} \), expressed in elementary charge unit \( e = \text{F/NA} \) \((\text{F – Faraday constant, NA} \ – \text{Avogadro’s constant)}\), and \( n_W \) \((\geq 0)\) is the mean number of water \((W = \text{H}_2\text{O})\) molecules attached to \( X_i^{Z_i} \). The known chemical formulas of the \( X_i^{Z_i} \) 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 \((\text{C mol/L})\), is added into \( V_0 \) mL of titrand D, containing a substance A \((\text{C mol/L})\). An advance of the titration \( B(C, V) \Rightarrow A(C, V) \), denoted briefly as \( B \Rightarrow A \), is characterized by the fraction titrated

\[
\Phi = \frac{C \cdot V}{C_0 \cdot V_0}
\]

That introduces a kind of normalization (independence on \( V_0 \) value) for titration curves, expressed by \( \text{pH} = \text{pH(\Phi)} \), and \( E = E(\Phi) \) for potential \( \text{E [V]} \) 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, \( N_i \) \((i = 1, 2, \ldots, J)\) 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 \( N_i \) molecules of \( \text{H}_2\text{O} \) and \( \text{N}_i \) species of i-th kind, \( X_i^{Z_i} n_W \) \((i=2,3,\ldots,l)\), denoted briefly as \( X_i^{Z_i} \), where \( n_W \equiv n_W \equiv n_W \text{H}_2\text{O} \). Molar concentration of the species \( X_i^{Z_i} n_W \) is denoted as \( X_i^{Z_i} \). Except the \( \text{pH} = \text{pH(\Phi)} \), and \( E = E(\Phi) \) relationships, the D+T systems are represented graphically by speciation curves \( \log \left[ X_i^{Z_i} \right] = \phi(\Phi) \).

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 \((\text{for Br})\) and 1 \((\text{for HBrO or NaBrO})\) \((-1, 5)\). There are possible transitions between different bromine species, associated with changes of the oxidation states of this element, (Figure 1).
We consider first two D+T systems: (S1) NaOH → Br₂ and (S2) NaOH → HBrO. In the system S1, V₀ mL of D is composed of Br₂ (N₀₁ molecules) + H₂O (N₀₂ molecules), and V mL of T is composed of NaOH (N₀₃ molecules) + H₂O (N₀₄ molecules). In the system S2, V₀ mL of D is composed of HBrO (N₀₁ molecules) + H₂O (N₀₂ molecules), and V mL of T is composed of NaOH (N₀₃ molecules) + H₂O (N₀₄ molecules).

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

\[ \text{H}_2\text{O} (\text{N}_1), \text{H}^+1 (\text{N}_2, \text{n}_2), \text{OH}^-1 (\text{N}_3, \text{n}_3), \text{HBrO}_3 (\text{N}_4, \text{n}_4), \text{BrO}_3^- (\text{N}_5, \text{n}_5), \text{Br}^-1 (\text{N}_6, \text{n}_6), \text{Br}_2 (\text{N}_8, \text{n}_8), \text{Br}_3^- (\text{N}_9, \text{n}_9), \text{BrO}^- (\text{N}_7, \text{n}_7) \]

Let us assume that V mL of the titrant T is added into V₀ mL of the titrand D, up to a given point of the titration, and V₀ + V mL of D+T mixture is obtained. Molar concentration (C₀) of the solute X in solution, or (S2) HBrO (C₀) solution, and we have

\[ \text{C}_0 \cdot V_0 = 10^3 \cdot \text{N}_01 / \text{N}_A \]  

(3)

and molar concentration (C) of the solute Y = NaOH in T is involved in relation

\[ \text{C} \cdot V = 10^3 \cdot \text{N}_03 / \text{N}_A \]  

(4)

Molar concentrations \([X_i^{\text{Z}_i}]\) of the species in the D+T mixture are involved in the relations

\[ [X_i^{\text{Z}_i}] \cdot V_i = 10^3 \cdot \text{N}_i / \text{N}_A \]  

(5)

At V=0, the related system is limited to D, i.e. (S1) Br₂ (C₀) solution, or (S2) HBrO (C₀) solution, and we have

\[ [X_i^{\text{Z}_i}] \cdot V = 10^3 \cdot \text{N}_i / \text{N}_A \]  

(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**

V₀ mL of D is composed of Br₂ (N₀₁ molecules) + H₂O (N₀₂ molecules), and V mL of T is composed of NaOH (N₀₃ molecules) + H₂O (N₀₄ molecules). The balances related to the D+T mixture are as follows:

\[ f_1 = \text{CHB} \]

\[ \text{N}_2 - \text{N}_3 - \text{N}_7 - \text{N}_9 - \text{N}_{10} + \text{N}_{11} = 0 \]  

(7)

\[ f_2 = f(H) \]

\[ 2N + N_1(1+2n) + N_1(1+2n) + N_1(1+2n) + 2N_8n_8 + N_1(1+2n) + 2N_1n_1 + 2N_1n_1 + 2N_1n_1 + 2N_1n_1 + 2N_1n_1 = 2N_{12} + 2N_{14} \]  

(8)

\[ f_3 = f(O) \]

\[ N_1 + N_1n_1 + N_1(1+n_1) + N_1(3+n_1) + N_1(3+n_1) + N_1(1+n_1) + N_1n_1 + N_1n_1 + N_1n_1 + N_1n_1 + N_1n_1 \]

(9)

\[ f_4 = f(Br) \]

\[ N_1 + N_1 + N_1 + 2N_4 + 3N_8 + N_{10} = 2N_{13} \]  

(10)

\[ \frac{-f_3}{f_4} \rightarrow f(Na) \]

\[ N_{03} = N_{11} \]  

(11)

Note, for example, that N₁ molecules (z₁=0) of HBrO₂ₙ₁H₂O involve: N₁(1+2n₁) atoms of H, N₁(3+n₁) atoms of O, and N₁ atoms of Br. From Equations 8 and 9 we have

\[ f_{12} = 2f_2 - f_3 : - N_8 + N_9 + 5N_4 + 6N_8 + N_4 + 2N_8 = 2N_{13} \]  

(12)

From Equations 7, 11 and 12

\[ f_{12} + f_3 - f_4 : \quad 5N_4 + 5N_8 + N_6 - N_9 - N_{10} = 0 \]  

(13)

Applying the atomic number \(Z_{ne} (=35)\) for Br, from Equations 10 and 11 we have

\[ Z_{ne} \cdot f_{12} - (f_3 + f_4 - f_12) : (Z_{ne} -5)(N_4 + N_8) + (Z_{ne} -1)(N_6 + N_8) + 2Z_{ne}N_4 + (3Z_{ne} +1)N_6 + (Z_{ne} +1)N_8 = Z_{ne}N_{01} \]  

(14)

Note, for example, that \(f_1 = f(Na) \leftrightarrow f(Na) = f_1 = -f(Na)\).

**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 V₀ mL of D is comprised of HBrO (N₀₁ molecules) + H₂O (N₀₂ molecules), and V mL of T is composed of NaOH (N₀₃ molecules) + H₂O (N₀₄ molecules). The \(f_1 = \text{CHB}\) in the system S2 is identical with Equation 7, and \(-f_3 = f(Na)\) as in Equation 11. Then after formulation of the balances for the related D+T mixture:

\[ f_1 = f(H) : \]

\[ 2N + N_1(1+2n) + N_1(1+2n) + N_1(1+2n) + 2N_8n_8 + N_1(1+2n) + 2N_1n_1 + 2N_1n_1 + 2N_1n_1 + 2N_1n_1 + 2N_1n_1 = 2N_{12} + 2N_{14} \]  

(15)

\[ f_2 = f(O) : \]

\[ N_1 + N_1n_1 + N_1(1+n_1) + N_1(3+n_1) + N_1(3+n_1) + N_1(1+n_1) + N_1n_1 + N_1n_1 + N_1n_1 + N_1n_1 + N_1n_1 \]

(16)

\[ f_3 = f(Br) : \quad N_1 + N_1 + N_1 + 2N_4 + 3N_8 + N_{10} = 2N_{13} \]  

(17)

we have here, by turns,

\[ f_{12} = 2f_2 - f_3 : - N_8 + N_9 + 5N_4 + 6N_8 + N_4 + 2N_8 = 2N_{13} \]  

(18)

\[ f_{12} + f_3 - f_4 : 5N_4 + 5N_8 + N_6 - N_9 - N_{10} = 2N_{13} \]  

(19)
\[
Z_{\text{m}} \cdot f_{\text{i}}' - (f_{\text{j}}' + f_{\text{k}}') \cdot (Z_{\text{m}} - 5)(N_{\text{i}} + N_{\text{j}}) + (Z_{\text{m}} - 1)(N_{\text{j}} + N_{\text{k}}) + 2Z_{\text{m}}N_{\text{i}} + (3Z_{\text{m}} + 1)N_{\text{j}} + (Z_{\text{m}} + 1)N_{\text{k}} = (Z_{\text{m}} - 4)N_{\text{i}} \quad (20)
\]

In principle, the numbers \(N_{\text{m}}\) and \(N_{\text{i}}\) of the molecules composing the system S2 and the numbers \(N_{\text{j}}\) of the species in the related D+T mixture are different than that in the system S1.

### Components versus species

Br₂ and \(H_{2}O\) forming D, and NaOH and \(H_{2}O\) forming T, are components of the system S1; HBrO and \(H_{2}O\) forming D, and NaOH and \(H_{2}O\) 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

\[
[H^{+1}] - [OH^{-1}] - [BrO_{3}^{-1}] - [Br^{-1}] - [Br^{+1}] + [Na^{+1}] = 0 \quad (7a)
\]

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

\[
([HBrO_{3}]+[BrO_{3}^{-1}]) + ([HBrO]+[BrO_{3}^{-1}]) + 2[Br_{2}] + 3[Br^{-1}] + [Br^{+1}] = 2C_{0}V/(V_{0}+V) \quad (10a)
\]

\[
[Na^{+1}] = CV/(V_{0}+V) \quad (11a)
\]

\[5([HBrO_{3}]+[BrO_{3}^{-1}]) + ([HBrO]+[BrO_{3}^{-1}]) - [Br^{-1}] - [Br^{+1}] = 0 \quad (13a)
\]

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

\[
[H^{+1}] - [OH^{-1}] - [BrO_{3}^{-1}] - [Br^{-1}] - [Br^{+1}] + CV/(V_{0}+V) = 0 \quad (7b)
\]

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:

\[
([HBrO_{3}]+[BrO_{3}^{-1}]) + ([HBrO]+[BrO_{3}^{-1}]) + 2[Br_{2}] + 3[Br^{-1}] + [Br^{+1}] = C_{0}V/(V_{0}+V) \quad (17a)
\]

\[
5([HBrO_{3}]+[BrO_{3}^{-1}]) + ([HBrO]+[BrO_{3}^{-1}]) - [Br^{-1}] - [Br^{+1}] = C_{0}V/(V_{0}+V) \quad (19a)
\]

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: \(N_{\text{m}}\), \(n\) (\(i=2,…,I\)), and \(N_{\text{i}}\) related to \(W=H_{2}O\) molecules (i.e., free \(W\) as the species, \(W\) in hydrated species, and \(W\) as components) are cancelled within \(f_{\text{i}}\). In other words, I – 1 kinds of the species \(X_{\text{i}}^\pm \cdot n_{\text{W}}\) are involved in equations related to the system.

All \(n_{\text{W}}\) values are virtually unknown – even for \(X_{\text{i}}^\pm = H^{\pm}\) [14] in aqueous media, and depend on ionic strength \((I)\) of the solution. The species \(X_{\text{i}}^\pm \cdot n_{\text{W}}\) with different \(n_{\text{W}}\) values are considered equivalently. Also the \(X_{\text{i}}^\pm\)'s with different numbers of \(H_{2}O\) molecules involved, e.g. \(H_{4}IO_{6}^{-1}, IO_{4}^{-1}, HBR_{O}^{-1}, B(OH)_{3}^{-1}, AI_{O}^{-1}, AI(OH)_{2}^{-1}\) are considered equivalently, i.e., as the same species in this medium [11].

### The Approach I to GEB

In \(C_{g}\) 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 \(Br\) involve \(2Z_{Br}N_{01}\) 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∙1 + 1∙x + 3∙(−2) = 0 → \(x = 5\) for \(HBrO_{3}\); 1∙x + 3∙(−2) = −1 → \(x = 5\) for \(BrO_{3}^{-1}\); 1∙1 + 1∙x + 1∙(−2) = 0 → \(x = 1\) for \(HBrO\); 3∙x = −1 → \(x = −1/3\); 1∙x = −1 → \(x = −1\) for \(Br^{+1}\).

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 \(HBrO_{3}\) 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]:

\(N_{g}\) species \(HBrO_{n} \cdot nH_{2}O\) involve \((Z_{Br}−5)\cdot n\) bromine electrons;

\(N_{s}\) species \(BrO_{3}^{-1} \cdot nH_{2}O\) involve \((Z_{Br}−5)\cdot n\) bromine electrons;

\(N_{w}\) species \(HBrO_{n} \cdot nH_{2}O\) involve \((Z_{Br}−5)\cdot n\) bromine electrons;

\(N_{t}\) species \(BrO_{3}^{-1} \cdot nH_{2}O\) involve \((Z_{Br}−5)\cdot n\) bromine electrons;

\(N_{l}\) species \(Br^{-1} \cdot nH_{2}O\) involve \((3Z_{Br}−1)\cdot n\) bromine electrons;

\(N_{i}\) species \(Br^{-1} \cdot nH_{2}O\) involve \((3Z_{Br}−1)\cdot n\) bromine electrons;

\(N_{m}\) molecules of \(Br\) involved \((2Z_{Br}−n)\cdot N_{01}\) bromine electrons.

### Equivalence of the Approaches I and II to GEB

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

\[
(Z_{Br}−5)((HBrO_{3})+[BrO_{3}^{-1}]) + (Z_{Br}−1)((HBrO)+[BrO_{3}^{-1}]) + 2Z_{Br}[Br_{2}] + (3Z_{Br}−1)[Br^{-1}] + (Z_{Br}−1)[Br^{+1}] = 2Z_{Br}C_{0}V/(V_{0}+V) \quad (14a)
\]

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

\[
(Z_{Br}−5)((HBrO_{3})+[BrO_{3}^{-1}]) + (Z_{Br}−1)((HBrO)+[BrO_{3}^{-1}]) + 2Z_{Br}[Br_{2}] + (3Z_{Br}−1)[Br^{-1}] + (Z_{Br}−1)[Br^{+1}] = (Z_{Br}−1)C_{0}V/(V_{0}+V) \quad (20a)
\]

The equations: 14 + 14a and 20 + 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

\[ \text{Approach I to GEB} \iff \text{Approach II to GEB} \tag{21} \]

is true \[10\].

Other equivalent forms of GEB

The \( f_{12} \) (Equation 18) and other combinations of \( f_{i} \) with \( f_{0} \) and \( f_{1} \) (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

\[ -[H^{+1}] + [OH^{-1}] + 5[HBrO_{3}^{-}] + 6[BrO_{3}^{-}] + [HBrO] + 2[BrO^{2-}] = \frac{CV}{(V_{0}+V)} \tag{12a} \]

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

\[ -[H^{+1}] + [OH^{-1}] + 5[HBrO_{3}^{-}] + 6[BrO_{3}^{-}] + [HBrO] + 2[BrO^{2-}] = \frac{CV}{(V_{0}+V)} + \frac{CV}{(V_{0}+V)} \tag{18a} \]

One can also state that \( f_{12} \) (Equation 12) and other combinations of the \( f_{i} \), with \( f_{0} \) and \( f_{1} \) (Equations 7,10,11) have full properties of GEB for the S1 system. For example, we have:

\[ (f_{12} + f_{0} + f_{1} - f_{2})/2 : 3(N_{s} + N_{2}) + N_{s} + N_{2} + N_{s} + N_{s} = N_{o} \rightarrow (22) \]

\[ 3([HBrO_{3}^{-}] + [BrO_{3}^{-}]) + [HBrO] + [BrO^{2-}] + [Br] + [Br^{-}] = \frac{CV}{(V_{0}+V)} \tag{22a} \]

For the system S2, the relations derived for \( (f_{12} + f_{0} + f_{1} - f_{2})/2 \) are identical with equations 22 and 22a.

Minimal number of constituents as a criterion of GEB simplicity

As were stated above, \( f_{12}, f_{12} + f_{0}, \ldots \) and any linear combination of \( f_{12} \) with \( f_{0}, f_{2}, \ldots \) related to the system in question, i.e.,

\[ f = f_{12} + a_{0}f_{0} + \sum_{k=3}^{K} a_{k}f_{k} \text{ (where } a_{k} \in R \text{ for } k=0,3,4,\ldots,K) \tag{23} \]

Have full properties of GEB. An interesting matter is here the selection of such \( a \) coefficients where the linear combination contains the minimal number of constituents (species, components), after all cancellations done in (23). We calculate the summary number \( S_{n} = I_{n} + I_{n} \) of constituents in Equation (23), where \( I_{n} \) the number of species, and \( I_{n} \) the number of components. We refer here to the systems S1 and S2.

For the system S1 we have: \( S_{0} = 6+4+0 = 6 \) from (13a), \( S_{1} = 7+1 = 8 \) from (14a), \( S_{0} = 6+1+7 = 14 \) from (12a), \( S_{0} = 6+1+7 = 14 \) from (22a). For the system S2 we have: \( S_{0} = 6+1+1+7 = 14 \), \( S_{0} = 7+1+8 \) from (19a), \( S_{0} = 6+2+8 = 16 \) from (18a), \( S_{0} = 6+1+7 = 14 \) from (22a). Then we have minimal \( S_{0} \) for the system S1, and \( S_{0} \) for the system S2. The linear combinations with smaller number \( S_{0} \) are not obtainable for the systems S1 and S2 and then \( S_{0} \) is 0 in both instances, i.e., the combination (23) is not transformed there to identity 0 = 0. Note that \( I_{n} \)'s in (12a) and (18a) involve 2 components related to the species (\( H^{+1},N_{s},OH^{-1},N_{s},\) 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 or (S2) HBrO, i.e. 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 in S1 or HBrO in S2 are characterized as ‘distributors’ of electrons in the related systems. Note that Br and HBrO do not oxidize water molecules, i.e., products of H2O 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; \( N_{s} + N_{2} = -N_{s} - N_{2} \) 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 Br2 (C0) and expressed by Equation 13a, obtained according to Approach II to GEB, can be rewritten as follows:

\[ 1+(+1)\cdot([HBrO_{3}^{-}]+[BrO^{2-}]) + 1+(+1)\cdot([HBrO]+[BrO^{2-}]) + 2\cdot0\cdot[Br_{2}] + 3\cdot(1-3)\cdot[Br]^{-1} + 1\cdot(1)\cdot[Br^{-}] = 2\cdot(0)\cdot C_{0}\cdot(V_{0}+V) \tag{13b} \]

Whereas the GEB related to the system S2 with HBrO (C0) and expressed by Equation 19a, obtained according to Approach II to GEB, can be rewritten as follows:

\[ 1+(+1)\cdot([HBrO_{3}^{-}]+[BrO^{2-}]) + 1+(+1)\cdot([HBrO]+[BrO^{2-}]) + 2\cdot0\cdot[Br_{2}] + 3\cdot(1-3)\cdot[Br]^{-1} + 1\cdot(1)\cdot[Br^{-}] = 1+(+1)\cdot C_{0}\cdot(V_{0}+V) \tag{19b} \]

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 (Br2 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. \(-[Br]^{-1} = (-1)[Br]^{-1}= 3\cdot(1-3)\cdot[Br]^{-1}\) in Equation 13a or 19a, where \(3 = \text{number of Br-atoms, } -1/3 = \text{oxidation number of Br in Br}^{-1}\).

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 \textit{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\(^{+1}\)), whereas an equation for concentration balance involves more species, see Equations 10a or 17a. In the equality (11a), the value for [Na\(^{+1}\)] is a number for the pre-assumed C and V\(_c\) 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 \(E_0\), and other equilibrium constants 

\[
K_1 \ = \ \frac{[H^+]\cdot[H_2O]}{[H^+][H_2O]}
\]

\[
K_2 \ = \ \frac{[OH^-][H_2O]}{[H^+][H_2O]}
\]

\[
K_3 \ = \ \frac{[H_2O]}{[H^+]\cdot[OH^-]}
\]

\[
K_4 \ = \ \frac{[H^+]\cdot[OH^-]}{[H_2O]} 
\]

which are involved in the calculation of 

\[
\Delta G = -nFE
\]

and 

\[
\text{pH} = -\log[H^+] 
\]

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 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]:

\[
[H^+] = 10^{11.4} \cdot [OH^-] = 10^{14.2} \cdot [BrO_4^-] = 10^{9} \cdot [BrO_3^-] \cdot [Br^+] 
\]

\[
[Br_2] = 10^{11} \cdot [BrO^-] \cdot [BrO_3^-] \cdot [BrO_4^-] = 10^{2} \cdot [BrO^-] \cdot [BrO_4^-] 
\]

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

\[
A\cdot x = -log\text{e} \cdot E, \ -log[H^+] \cdot \text{pH} \ -log[Br^+] \cdot \text{pBr} \]

Three independent variables: \(x^T = (E, \text{pH}, \text{pBr})\) 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: \([e^+] = 10^{1.5}, [H^+] = 10^{14}, [Br^-] = 10^{14}\), where \(1/A = R/T/F/\text{In}10; A = 16.9\) 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 \(E_0\) values were taken from references [15-18].

In Table 1 (numbers 5,10,15) we have also the data involved with liquid bromine, \(Br_2\). Solubility of \(Br_2\) is 35 g/L (20 \(^\circ\)C) [19], i.e. \(s = 0.22\) mol/L > \(C_0 = 10^{-2}\) mol/L, and then \([Br_2] = 0\) in the systems S1, S2. \(HBrO_3\) 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 \(K_a\) and \(E_{0B}\) for reaction \(BrO_4^- + 3H_2O + 5e^- = \frac{1}{2} Br_2 + 6OH^-\). From \(K_{2a}\) and \([BrO_4^-]\cdot[OH^-]^2 = K_a\cdot[BrO_4^-][e^-]^2\) we have, by turns: \(K_{w} = K_a\cdot[BrO_4^-]^2 \cdot log_k = log_{k5} = 6pK_w - 5AE_{05} = 5AE_{02B} - 6pK_w\); the value \(E_{06} = 1.482\) - 6.14/(5.169-1) = 0.4879 = 0.50 V in Table 1.

On the basis of \(E_{011} = 0.68\) V for \(BrO_2^-/Br^+\) pair at \(pH = 14\) [22] and \(K_{w}\), we calculate \(K_{a}\) and then \(E_{0B}\) for \(BrO_2^- + 8H^+ + 8e^- \rightarrow Br^+ + 4H_2O\). For \(BrO_2^- + 4H_2O + 8e^- \rightarrow Br^+ + 8OH^-\) we have \([BrO_4^-][OH^-]^2 = K_a\cdot[BrO_4^-][e^-]^2\); then \(K_a = K_{w}/(K_{a})^2 \rightarrow log_k = log_{k17} - 8pK_w + 8AE_{0}\) \(AE_{0} = 8AE_{017} + 8pK_w \rightarrow E_{07} = 0.68 + 14/16.9 = 1.5084\ V.

On the basis of \(E_{013}\) and \(E_{015}\) (Table 1) we calculate \(K_{a}\) and \(E\) for the reaction \(BrO_4^- + 8H^+ + 8e^- \rightarrow Br^+ + 4H_2O\) we get \(E_{05} = 0.25\) - 0.14/1.243 = 1.5035 = 1.5084 V.

On the basis of Table 1 we obtain, by turns: \((K_a)^2/2pKW = K_{14} \rightarrow 2logK_{a} - 2logK_{14} \rightarrow 2logK_{a} = 2logK_{12} + logK_{14} \rightarrow 2AE_{07} = 2.5AE_{017} + 2AE_{015} \rightarrow E_{07} = (5E_{017} + 3E_{015})/6 = (5\cdot1.513 + 1.098)/6 = 1.4438 \ V = E_{017}, E_{015}\).

In the links we do not find the \(pK_{17}\) values for \(HBrO = H^+ + BrO^-\), \(K_{17} = [H^+]\cdot[BrO^-]/[HBrO]\). However, we can find it on the basis of relations:

\[
(a) pK_{17} = log_{K_{17}} = log_{K_{14}} + 2pKW; \text{e.g. (a1) pK}_{17} = 2.169; (E_{012} - E_{013}) + 2.14 = 8.734; (a2) pK_{17} = 2.169; (E_{012} - E_{013}) + 2.14 = 8.903; (a3) pK_{17} = 2.169; (E_{012} - E_{013}) + 2.14 = 8.700; \\
(b) pK_{17} = log_{K_{17}} - 0.5log_{K_{14}} - log_{K_{12}} + 2pKW; \text{e.g. (b1) pK}_{17} = 16.9; (E_{012} - E_{014} - E_{013}) + 2.14 = 8.734; (b2) pK_{17} = 16.9; (E_{012} - E_{014} - E_{013}) + 2.14 = 8.751; (b3) pK_{17} = 16.9; (E_{012} - E_{013} - E_{014}) + 2.14 = 8.712; etc.\]

The \(E_0\) values calculated on the basis of \(E_0\) values are not far distant from the \(pK_{17}\) 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 \(E_0\). 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<sub>0</sub>) values are expressed in SHE scale.

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<td>1</td>
<td>BrO&lt;sup&gt;-1&lt;/sup&gt; + 2H&lt;sup&gt;+&lt;/sup&gt; + 2e&lt;sup&gt;-&lt;/sup&gt; = BrO&lt;sup&gt;3-&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>[BrO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-1&lt;/sup&gt; = K&lt;sub&gt;e1&lt;/sub&gt;[BrO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-1&lt;/sup&gt;[H&lt;sup&gt;+&lt;/sup&gt;]&lt;sup&gt;2&lt;/sup&gt;[e&lt;sup&gt;-&lt;/sup&gt;]&lt;sup&gt;2&lt;/sup&gt;</td>
<td>E&lt;sub&gt;01A&lt;/sub&gt; = 1.745</td>
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<td>2</td>
<td>BrO&lt;sup&gt;-1&lt;/sup&gt; + 6H&lt;sup&gt;+&lt;/sup&gt; + 5e&lt;sup&gt;-&lt;/sup&gt; = ½ Br&lt;sub&gt;2&lt;/sub&gt; + 3H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>[Br&lt;sub&gt;2&lt;/sub&gt;] = K&lt;sub&gt;e2&lt;/sub&gt;[BrO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-1&lt;/sup&gt;[H&lt;sup&gt;+&lt;/sup&gt;]&lt;sup&gt;6&lt;/sup&gt;[e&lt;sup&gt;-&lt;/sup&gt;]&lt;sup&gt;5&lt;/sup&gt;</td>
<td>E&lt;sub&gt;02A&lt;/sub&gt; = 1.482</td>
<td>E&lt;sub&gt;02B&lt;/sub&gt; = 1.452</td>
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<td>3</td>
<td>BrO&lt;sup&gt;-1&lt;/sup&gt; + 5H&lt;sup&gt;+&lt;/sup&gt; + 4e&lt;sup&gt;-&lt;/sup&gt; = HBrO + 2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>[BrO&lt;sup&gt;-1&lt;/sup&gt;][OH&lt;sup&gt;-1&lt;/sup&gt;] = K&lt;sub&gt;e4&lt;/sub&gt;[BrO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-1&lt;/sup&gt;[e&lt;sup&gt;-&lt;/sup&gt;]&lt;sup&gt;4&lt;/sup&gt;</td>
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<td>4</td>
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<td>[BrO&lt;sup&gt;-1&lt;/sup&gt;][OH&lt;sup&gt;-1&lt;/sup&gt;] = K&lt;sub&gt;e5&lt;/sub&gt;[BrO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-1&lt;/sup&gt;[e&lt;sup&gt;-&lt;/sup&gt;]&lt;sup&gt;5&lt;/sup&gt;</td>
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<td>E&lt;sub&gt;04B&lt;/sub&gt; = 0.54</td>
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<td>BrO&lt;sup&gt;-1&lt;/sup&gt; + 3H&lt;sub&gt;2&lt;/sub&gt;O + 5e&lt;sup&gt;-&lt;/sup&gt; = ½ Br&lt;sub&gt;2&lt;/sub&gt; + 6OH&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>[Br&lt;sub&gt;2&lt;/sub&gt;] = K&lt;sub&gt;e6&lt;/sub&gt;[BrO&lt;sub&gt;3&lt;/sub&gt;]&lt;sup&gt;-1&lt;/sup&gt;[H&lt;sup&gt;+&lt;/sup&gt;]&lt;sup&gt;6&lt;/sup&gt;[e&lt;sup&gt;-&lt;/sup&gt;]&lt;sup&gt;5&lt;/sup&gt;</td>
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<td>6</td>
<td>HBrO + H&lt;sup&gt;+&lt;/sup&gt; + e&lt;sup&gt;-&lt;/sup&gt; = ½ Br&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>[Br&lt;sub&gt;2&lt;/sub&gt;] = K&lt;sub&gt;e7&lt;/sub&gt;[HBrO][H&lt;sup&gt;+&lt;/sup&gt;][e&lt;sup&gt;-&lt;/sup&gt;]&lt;sup&gt;6&lt;/sup&gt;</td>
<td>E&lt;sub&gt;06A&lt;/sub&gt; = 0.613</td>
<td>E&lt;sub&gt;06B&lt;/sub&gt; = 0.61</td>
<td>E&lt;sub&gt;06C&lt;/sub&gt; = 0.61</td>
<td>E&lt;sub&gt;06D&lt;/sub&gt; = 0.61</td>
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<td>7</td>
<td>HBrO + H&lt;sup&gt;+&lt;/sup&gt; + 2e&lt;sup&gt;-&lt;/sup&gt; = Br&lt;sup&gt;-1&lt;/sup&gt; + H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>[Br&lt;sub&gt;-1&lt;/sub&gt;] = K&lt;sub&gt;e8&lt;/sub&gt;[HBrO][H&lt;sup&gt;+&lt;/sup&gt;][e&lt;sup&gt;-&lt;/sup&gt;]&lt;sup&gt;2&lt;/sup&gt;</td>
<td>E&lt;sub&gt;07A&lt;/sub&gt; = 1.574</td>
<td>E&lt;sub&gt;07B&lt;/sub&gt; = 1.6</td>
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<td>8</td>
<td>2BrO&lt;sup&gt;-1&lt;/sup&gt; + 2H&lt;sub&gt;2&lt;/sub&gt;O + 2e&lt;sup&gt;-&lt;/sup&gt; = Br&lt;sub&gt;2&lt;/sub&gt; + 4OH&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>[Br&lt;sub&gt;2&lt;/sub&gt;][OH&lt;sup&gt;-1&lt;/sup&gt;] = K&lt;sub&gt;e12&lt;/sub&gt;[BrO&lt;sub&gt;3&lt;/sub&gt;][e&lt;sup&gt;-&lt;/sup&gt;]&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>Br&lt;sup&gt;-1&lt;/sup&gt; + H&lt;sup&gt;+&lt;/sup&gt; + 2e&lt;sup&gt;-&lt;/sup&gt; = 2Br&lt;sup&gt;-1&lt;/sup&gt;</td>
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<td>E&lt;sub&gt;09B&lt;/sub&gt; = 1.0873</td>
<td>E&lt;sub&gt;09C&lt;/sub&gt; = 1.087</td>
<td>E&lt;sub&gt;09D&lt;/sub&gt; = 1.087</td>
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<td>[Br&lt;sup&gt;-1&lt;/sup&gt;] = K&lt;sub&gt;e16&lt;/sub&gt;[Br&lt;sup&gt;-1&lt;/sup&gt;][e&lt;sup&gt;-&lt;/sup&gt;]&lt;sup&gt;3&lt;/sup&gt;</td>
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<td>E&lt;sub&gt;11B&lt;/sub&gt; = 1.05</td>
<td>E&lt;sub&gt;11C&lt;/sub&gt; = 1.05</td>
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<td>HBrO&lt;sub&gt;2&lt;/sub&gt; + H&lt;sup&gt;+&lt;/sup&gt; + Br&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>[H&lt;sup&gt;+&lt;/sup&gt;][BrO&lt;sup&gt;-1&lt;/sup&gt;] = K&lt;sub&gt;11&lt;/sub&gt;[HBrO]</td>
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<td>[H&lt;sup&gt;+&lt;/sup&gt;][OH&lt;sup&gt;-1&lt;/sup&gt;] = K&lt;sub&gt;11&lt;/sub&gt;[H&lt;sub&gt;2&lt;/sub&gt;O]</td>
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<td>pK&lt;sub&gt;11D&lt;/sub&gt; = 14.0</td>
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Note: logK<sub>k</sub> = n<sub>k</sub>A; E<sub>0k</sub> = 16.9; pK<sub>51</sub> = -logK<sub>51</sub>; pK<sub>11</sub> = -logK<sub>11</sub>; pK<sub>51</sub> = -logK<sub>51</sub>

The same stoichiometric reactions. However, based on the E<sub>0</sub> 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 $K_{13D} = (K_{e6D})^2/(K_{e4D})^2 \rightarrow \log K_{13D} = 2\log K_{e6D} - \log K_{e4D} \rightarrow 2AE_{013D} = 2\cdot5AE_{06D} - 2\cdot4AE_{04D} \rightarrow E_{013D} = 5E_{06D} - 4E_{04D} = 5\cdot0.5 - 4\cdot0.54 = 0.34 \neq 0.45$; 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

```matlab
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-Br2-Br3-BrO-BrO3);
%Concentration balance for Br (Br+3Br2+2Br3+HBrO+BrO+HBrO3+BrO3-2*C*V/(V0+V));
%Electron balance ((ZBr+1)*Br+(3*ZBr+1)*Br2+2*ZBr*Br3+(ZBr-1)*(HBrO+BrO)...+
+(ZBr-5)*(HBrO3+BrO3)-2*ZBr*C*V/(V0+V));

yy(1)=log10(Br);
yy(2)=log10(Br2);
yy(3)=log10(Br3);
yy(4)=log10(HBrO);
yy(5)=log10(HBrO3);
yy(6)=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 ($\Phi$, 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: $E = E(\Phi)$ and $pH = pH(\Phi)$ for the systems S1 and S2 are presented in Figure 2 together with speciation diagrams, where the curves $\log[c_\Phi] - \phi(\Phi)$ were plotted for different bromine species (Table 2).

Before 2006, the basic property of the balance $2\dot{f}(O) - \dot{f}(H)$ for redox systems was unknown at all in the scientific world, and the linear independency/dependency of $2\dot{f}(O) - \dot{f}(H)$ 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 Michałowski, 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 Michałowski.

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 \textit{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
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 $f_{12} = 2f(O) - f(H)$ with charge balance $f_0 = ChB$ and other elemental/core balances $f_k = f(Y_k)$ (k=3,…,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 $f_0,f_3,…,f_K$ when related to non-redox systems. In other words, the set of K independent balances $f_0,f_{12},f_3,…,f_K$ is applied to a non-redox system with K-2 independent elemental/core balances $f_k = f(Y_k)$ for $Y_k \neq H, O$. 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-
other words, elemental balances: the emanation of balances for H and O, referred to aqueous media. Let’s repeat: the GEB concept, valid for redox electrolytic systems, is the unique role of H and O in redox systems, suggested in earlier oxidation numbers are involved. On the other hand, it points to partial reactions, where the species of the same element with different free electrons in elementary redox reactions, as described in half- or electron concentrations in redox systems, deny the unique role of purpose. This fact, especially the simple calculations [9] of free solvent media [28-30].

The difference between redox and non-redox systems is then ‘coded’ in $f_i$. This unique, general property explains clearly why the elemental balances $f_i^+$ and $f_i^-$ are not formulated for non-redox systems, of any degree of complexity. The $f_i^+$ and any linear combination of $f_i$, with $f_i^+$, $f_i^-$ for a given system retain full properties of the GEB. In other words, $f_i^+$ is fully compatible with other ($f_i^+$, $f_i^-$) 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.

References


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