



# Some Regularities Inherent in the Balance $2 \cdot f(O) - f(H)$ Formulated for an Electrolytic System with Symproportionation Reactions Involved

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## Abstract

The general properties of the balance  $f_{12} = 2 \cdot f(O) - f(H)$ , as the linear combination of elemental balances:  $f_1 = f(H)$  for H and  $f_2 = f(O)$  for O, formulated for electrolytic systems, are presented. These properties/regularities are inherently related to linear combination (LC) of  $f_{12}$  with charge ( $f_0$ ) and other elemental/core balances  $f_k = f(Y_k)$  ( $Y_k \neq H, O$ ), expressed by  $LC = \sum_{k=1}^K d_k \cdot f_k - f_0$ , where the multipliers  $d_k$  are involved with oxidation numbers (ONs) of the elements in the system in question. The linear dependence or independence of  $f_{12}$  from  $f_0, f_3, \dots, f_K$ , expressed by LC, provides the general criterion distinguishing between non-redox and redox systems. The  $f_{12}$  is the primary form of Generalized electron balance (GEB), completing the set of K independent balances  $f_0, f_{12}, f_3, \dots, f_K$  needed for the solution of a redox system according to GATES/GEB principles. For the solution of a non-redox system, the set of K-1 independent equations  $f_0, f_3, \dots, f_K$  is required. In this formulation, the terms: ONs, oxidant, reductant, and equivalent mass are derivative/redundant concepts. These properties/regularities of  $f_{12}$  are illustrated here by a redox system where symproportionation reactions occur.

**Keywords:** Thermodynamics of electrolytic systems; Generalized approach to electrolytic systems (GATES); Generalized electron balance (GEB); Redox titrations.

**Notations:** D – titrand (solution titrated), LC – linear combination, ON – oxidation number, T – titrant, V – volume [mL] of T,  $V_0$  – volume [mL] of D.

**Motto:** *Everything should be made as simple as possible, but not simpler* (A. Einstein).

## 1. Introduction

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, formulated for electrolytic redox and non-redox systems in aqueous media, is put in context with charge ( $f_0 = ChB$ ) and elemental/core balances  $f_k = f(Y_k)$  for  $Y_k \neq H, O$  ( $k=3, \dots, K$ ), according to Generalized approach to redox systems (GATES) principles formulated (1992) by Michałowski [1, 2]. For this purpose, the linear combination  $LC = \sum_{k=1}^K d_k \cdot f_k - f_0$  is formulated, where  $d_k$  ( $k=1, \dots, K$ ) are the oxidation numbers (ONs) for  $Y_1=H$ ,  $Y_2=O$ , and  $Y_k$  ( $k=3, \dots, K$ ). For a non-redox system, the LC is expressed by identity,  $0=0$ , i.e.,  $f_{12}$  is linearly dependent on  $f_0, f_3, \dots, f_K$ , and then  $f_{12} = \sum_{k=3}^K d_k \cdot f_k - f_0$ . Therefore, formulation of a non-redox system is realized with use of K-1 independent balances  $f_0, f_3, \dots, f_K$ .

The core is perceived as a non-transformable (in a given system) cluster of atoms, of the same elemental composition (expressed by chemical formula) and structure; e.g. the set of species:  $HSO_4^{-1} \cdot n_{13W}$  and  $SO_4^{-2} \cdot n_{14W}$  in Eq. 12 contains  $SO_4^{-2}$  as the core.

For a redox system, LC is expressed by equation different from the identity  $0=0$ , i.e.,  $f_{12}$  completes the set of K independent balances  $f_0, f_{12}, f_3, \dots, f_K$  necessary for thermodynamic solution of a redox system. The linear dependence/independence of  $f_{12}$  from  $f_0, f_3, \dots, f_K$  is thus the general criterion distinguishing between non-redox and redox systems, of any degree of complexity. In a redox system, the  $f_{12}$  is the primary form of Generalized electron balance (GEB),  $f_{12} = pr\text{-GEB}$ , formulated according to Approach II to GEB, and applied for solution of electrolytic redox systems according to GATES/GEB principles. The set  $f_0, LC, f_3, \dots, f_K$  is usually applied for this purpose, instead of the set  $f_0, f_{12}, f_3, \dots, f_K$ .

The Approach II to GEB (formulated 2005) was preceded by the Approach I to GEB (formulated 1992). Both approaches – discovered by Michałowski – are equivalent: Approach I to GEB  $\Leftrightarrow$  Approach II to GEB. Formulation of GEB according to Approach I can be perceived in convention of card game, based on the common pool of electrons as money, introduced by electron-active elements, named as players; electron-non-active elements are

called there as fans [3]. The GEB is perceived as the Law of Nature, and GATES/GEB  $\subset$  GATES is considered as the best thermodynamic approach to redox systems.

The prior knowledge of oxidation numbers (ONs) for all elements of the system in question is not needed in the Approach II to GEB – contrary to the Approach I to GEB, where the knowledge of ONs for players is required.

All the regularities involved with  $f_{12} = 2 \cdot f(\text{O}) - f(\text{H})$  will be confirmed in examples presented below. Further generalizing comments will also be included.

## 2. Preliminary Assumptions and Notations

Redox reactions are usually referred to processes occurred during redox titrations. Since redox reactions are so important class of chemical reactions, we should know their physicochemical nature thoroughly, from titrimetric viewpoint [4-54].

Titration is considered as a kind of dynamic process, where  $V$  mL of titrant  $T$  is added, from the start up to a given point of the titration, into  $V_0$  mL of titrand  $D$ , and  $V_0 + V$  mL of  $D+T$  mixture is thus obtained, if the volumes additivity is valid/tolerable. The species formed in the  $D+T$  systems are involved in the related set of  $K+1$  balances:  $f_0, f_1, f_2, f_3, \dots, f_K$ , referred (for modelling purposes) to the closed system, separated from its environment by diathermal walls [1].

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  $\text{H}_2\text{O}$ , forming  $D = D(V_0)$  or  $T = T(V)$  in static, or  $D = D(V_0)$  and  $T = T(V)$  in dynamic  $D+T$  system. The  $D+T$  system thus obtained involves  $N_1$  molecules of  $\text{H}_2\text{O}$  ( $X_1^{z_1} = \text{H}_2\text{O}$ ,  $z_1=0$ ) and  $N_i$  species of  $i$ -th kind,  $X_i^{z_i} \cdot n_{iW}$  ( $i=2,3,\dots,I$ ), as hydrates denoted briefly as  $X_i^{z_i}$  ( $N_i, n_i$ ), where  $n_i \equiv n_{iW} \equiv n_i \text{H}_2\text{O}$  is a mean number of water ( $W=\text{H}_2\text{O}$ ) molecules attached to  $X_i^{z_i}$ ; the case  $n_{iW}=0$  is then also admitted;  $z_i = 0, \pm 1, \pm 2, \dots$  is the charge of  $X_i^{z_i}$ , expressed in terms of elementary charge unit  $e = F/N_A$  ( $F = 96485 \text{ C} \cdot \text{mol}^{-1}$  – Faraday's constant,  $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$  – Avogadro's number). For ordering purposes we assume:  $X_2^{z_2} \cdot n_{2W} = \text{H}^{+1} \cdot n_{2W}$ ,  $X_3^{z_3} \cdot n_{3W} = \text{OH}^{-1} \cdot n_{3W}$ , i.e.,  $z_2 = +1$ ,  $z_3 = -1$ . The  $n_i = n_{iW}$  values are virtually unknown, even for  $X_2^{z_2} = \text{H}^{+1}$  in aqueous media, and depend on ionic strength of the solution. The net charge of  $X_i^{z_i} \cdot n_{iW}$  equals to the charge of  $X_i^{z_i}$ :  $z_i + n_{iW} \cdot 0 = z_i$ .

Molar concentration of the species  $X_i^{z_i} \cdot n_{iW}$  is denoted as  $[X_i^{z_i}]$ ; for static  $D = D(V_0)$

$$[X_i^{z_i}] = 10^3 \cdot (N_i/N_A)/V_0 \quad (1)$$

and for a dynamic  $D+T$  system (volume  $V_0+V$ ) we have

$$[X_i^{z_i}] = 10^3 \cdot (N_i/N_A)/(V_0+V). \quad (2)$$

Electrolytic (redox and non-redox) systems are formulated according to the GATES principles [1]. For this purpose, the set of  $K+1$  balances  $f_0, f_1, f_2, f_3, \dots, f_K$  is obtained. The charged/ionic species  $X_i^{z_i} \cdot n_{iW}$  of the system are involved in the charge balance

$$f_0 = \sum_{i=2}^I z_i \cdot N_i = 0 \quad (3)$$

$$\sum_{i=2}^I z_i \cdot [X_i^{z_i}] = 0 \quad (3a)$$

applicable for static and dynamic systems. Note that  $0 \cdot [X_m] = 0$  for a species  $X_m \cdot n_{mW}$  with zero charge ( $z_m=0$ ), e.g.,  $0 \cdot [\text{H}_2\text{O}] = 0$  ( $z_1=0$ ).

Free water particles ( $N_1$ ), and water bound in the hydrates  $X_i^{z_i} \cdot n_{iW}$ , are included in the balances:  $f_1 = f(\text{H})$  and  $f_2 = f(\text{O})$ :

$$f_1 = f(\text{H}) = 2N_1 + \sum_{i=2}^I (a_{1i} + 2n_{iW}) \cdot N_i - \sum_{j=1}^J b_{1j} \cdot N_{0j} = 0 \quad (4)$$

$$f_2 = f(\text{O}) = N_1 + \sum_{i=2}^I (a_{2i} + n_{iW}) \cdot N_i - \sum_{j=1}^J b_{2j} \cdot N_{0j} = 0 \quad (5)$$

Next, the linear combination

$$f_{12} = 2 \cdot f_2 - f_1 = \sum_{i=2}^I (2 \cdot a_{2i} - a_{1i}) \cdot N_i - \sum_{j=1}^J (2 \cdot b_{2j} - b_{1j}) \cdot N_{0j} = 0 \quad (6)$$

is obtained, where  $a_{ki}$  and  $b_{kj}$  in Equations 4 – 6 are the numbers of atoms/cores  $Y_k$  ( $k=1,\dots,K$ ) in  $X_i^{z_i} \cdot n_{iW}$ , and in the  $j$ -th component of the system, resp.

The elemental/core balances:  $f_3, \dots, f_K$ , interrelating the numbers of atoms/cores  $Y_k \neq \text{H}, \text{O}$  in components and species, are as follows

$$f_k = f(Y_k) = \sum_{i=1}^I a_{ki} \cdot N_i - \sum_{j=1}^J b_{kj} \cdot N_{0j} = 0 \quad (k=3,\dots,K) \quad (7)$$

All the balances  $f_0, \dots, f_K$  are presented here as equations  $f_k = 0$ , see Equations 3 – 7.

In further parts of this paper, we concern on the procedure known in elementary algebra as linear combination. To avoid possible/simple mistakes, we apply the equivalent forms of balances/relations:

$$f_k = f(Y_k)$$

$$\sum_{i=1}^I a_{ki} \cdot N_i - \sum_{j=1}^J b_{kj} \cdot N_{0j} = 0 \Leftrightarrow \sum_{i=1}^I a_{ki} \cdot N_i = \sum_{j=1}^J b_{kj} \cdot N_{0j}$$

for elements with negative oxidation numbers, or

$$-f_k = -f(Y_k)$$

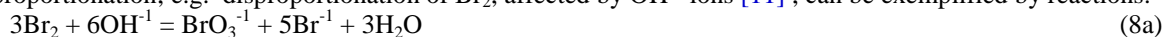
$$\sum_{j=1}^J b_{kj} \cdot N_{0j} - \sum_{i=1}^I a_{ki} \cdot N_i = 0 \Leftrightarrow \sum_{j=1}^J b_{kj} \cdot N_{0j} = \sum_{i=1}^I a_{ki} \cdot N_i$$

for elements with positive oxidation numbers,  $k \in 3, \dots, K$ . In this notation,  $f_k$  will be essentially treated not as the algebraic expression on the left side of the equation  $f_k = 0$ , but as an equation that can be expressed in alternative forms presented above.

For this purpose, we consider an example of titration  $T(V) \Rightarrow D(V_0)$  in a redox system  $\text{KBrO}_3 (\text{C}) \Rightarrow \text{NaBr} (\text{C}_0) + \text{H}_2\text{SO}_4 (\text{C}_{01})$ , where symproportionation [54] reactions occur.

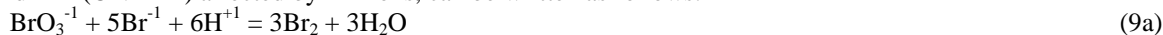
## 2.1. Symproportionation versus Disproportionation

Some elements form the species with at least three ONs; e.g. bromine (Br) [54] forms the species with five ONs (−1, −1/3, 0, 1, 5) in aqueous media. In particular, when Br species on an intermediate ON, e.g. Br<sub>2</sub> [17, 54], is transformed – simultaneously – to the Br-species with lower and higher ONs of this element, we are dealing with disproportionation; e.g. disproportionation of Br<sub>2</sub>, affected by OH<sup>−</sup> ions [11], can be exemplified by reactions:



Efficiencies of the reactions 18a,b are different [42].

In symproportionation, two species formed by the same element, here: Br with different ONs, react with formation of the species with intermediate ONs of this element. For example, symproportionation of BrO<sub>3</sub><sup>−</sup> (ON = 5) and Br<sup>−</sup> (ON = −1) affected by H<sup>+</sup> ions, can be written as follows:

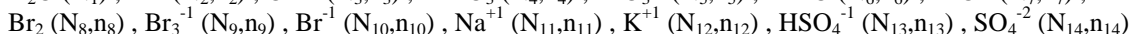
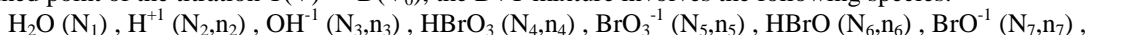


Disproportionation and symproportionation are then two mutually opposed redox reactions involved with the same element, here: Br.

The paper refers to dynamic (titration) redox systems where symproportionation of bromine species occur. The related systems are modeled according to principles assumed in the Generalized Approach to Electrolytic Redox Systems (GATES), with Generalized Electron Balance (GEB) concept involved in the GATES/GEB software. The results obtained from calculations made with use of iterative computer programs prepared according to MATLAB computational software, are presented graphically, as 2D graphs. On the basis of speciation curves, the reactions occurred in the systems were formulated, together with their relative efficiencies. The titrand (D) and titrant (T), as non-redox static subsystems of the dynamic redox D+T system, are also considered, for comparative purposes.

## 2.2. The Dynamic Redox System

Let us consider the D+T system, where D = D(V<sub>0</sub>) is composed of NaBr (N<sub>01</sub> molecules) + H<sub>2</sub>SO<sub>4</sub> (N<sub>02</sub> molecules) + H<sub>2</sub>O (N<sub>03</sub> molecules), and T = T(V) is composed of KBrO<sub>3</sub> (N<sub>04</sub> molecules) + H<sub>2</sub>O (N<sub>05</sub> molecules). At defined point of the titration T(V) ⇒ D(V<sub>0</sub>), the D+T mixture involves the following species:



Denoting  $C_0V_0 = 10^3 \cdot N_{01}/N_A$ ,  $C_{01}V_0 = 10^3 \cdot N_{02}/N_A$ ,  $CV = 10^3 \cdot N_{04}/N_A$ , we formulate the fraction titrated [4, 7, 25, 27, 38, 46]

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \quad (10)$$

It provides a kind of normalization in the related graphs (Figure 1), i.e., independence on V<sub>0</sub> value. Applying Eq. 2, the balances are written in terms of concentrations. The GEB related to this system can be resolved according to Approaches I and II.

## 3. Approach II to GEB in the System

Applying the Approach II to GEB, we have sequentially:

$$f_0 = \text{ChB}$$

$$N_2 - N_3 - N_5 - N_7 - N_9 - N_{10} + N_{11} + N_{12} - N_{13} - 2N_{14} = 0 \Rightarrow [\text{H}^+] - [\text{OH}^-] - [\text{BrO}_3^-] - [\text{BrO}^-] - [\text{Br}_3^-] - [\text{Br}^-] + [\text{Na}^+] + [\text{K}^+] - [\text{HSO}_4^-] - 2[\text{SO}_4^{2-}] = 0 \quad (11)$$

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

$$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(1+2n_6) + 2N_7n_7 + 2N_8n_8 + 2N_9n_9 + 2N_{10}n_{10} + 2N_{11}n_{11} + 2N_{12}n_{12} + N_{13}(1+2n_{13}) + 2N_{14}n_{14} = 2N_{02} + 2N_{03} + 2N_{05}$$

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

$$N_1 + N_2(1+n_2) + N_3(1+n_3) + N_4(3+n_4) + N_5(3+n_5) + N_6(1+n_6) + N_7(1+n_7) + N_8n_8 + N_9n_9 + N_{10}n_{10} + N_{11}n_{11} + N_{12}n_{12} + N_{13}(4+n_{13}) + N_{14}(4+n_{14}) = 4N_{02} + N_{03} + 3N_{04} + N_{05}$$

$$-f_3 = -f(\text{Na})$$

$$N_{01} = N_{11} \Rightarrow [\text{Na}^+] = C_0V_0/(V_0+V) \quad (12)$$

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

$$N_{04} = N_{12} \Rightarrow [\text{K}^+] = CV/(V_0+V) \quad (13)$$

$$-f_5 = -f(\text{SO}_4) = -f(\text{S})$$

$$N_{02} = N_{13} + N_{14} \Rightarrow [\text{HSO}_4^-] + [\text{SO}_4^{2-}] = C_{01}V_0/(V_0+V) \quad (14)$$

$$f_6 = f(\text{Br})$$

$$N_4 + N_5 + N_6 + N_7 + 2N_8 + 3N_9 + N_{10} = N_{01} + N_{04} \Rightarrow [\text{HBrO}_3] + [\text{BrO}_3^-] + [\text{HBrO}] + [\text{BrO}^-] + 2[\text{Br}_2] + 3[\text{Br}_3^-] + [\text{Br}^-] = (C_0V_0 + CV)/(V_0+V) \quad (15)$$

$$f_{12} = 2 \cdot f(\text{O}) - f(\text{H})$$

$$-N_2 + N_3 + 5N_4 + 6N_5 + N_6 + 2N_7 + 7N_{13} + 8N_{14} = 6N_{02} + 6N_{04} - [\text{H}^+] + [\text{OH}^-] + 5[\text{HBrO}_3] + 6[\text{BrO}_3^-] + [\text{HBrO}] + 2[\text{BrO}^-] + 7[\text{HSO}_4^-] + 8[\text{SO}_4^{2-}] = 6(C_{01}V_0 + CV)/(V_0+V) \quad (16)$$

$$f_{12} + f_0 - f_3 - f_4 - 6 \cdot f_5 = 0 \Leftrightarrow (+1)f_1 + (-2)f_2 + (+1)f_3 + (+1)f_4 + (+6)f_5 - f_0 = 0 \Leftrightarrow (+1)f(\text{H}) + (-2)f(\text{O}) + (+1)f(\text{Na}) + (+1)f(\text{K}) + (+6)f(\text{S}) - \text{ChB} = 0 \quad (17)$$

$$5(N_4+N_5) + 1(N_6+N_7) - N_9 - N_{10} = -N_{01} + 5N_{04} \quad \Rightarrow$$

$$5([HBrO_3] + [BrO_3^{-1}]) + [HBrO] + [BrO^{-1}] - [Br_3^{-1}] - [Br^{-1}] = -\frac{C_0V_0}{V_0+V} + 5\frac{CV}{V_0+V} \quad (17a)$$

$$(+5)([HBrO_3]+[BrO_3^{-1}]) + (+1)([HBrO]+[BrO^{-1}]) + 2\cdot 0\cdot [Br_2] + 3\cdot \left(-\frac{1}{3}\right)\cdot [Br_3^{-1}] + (-1)[Br^{-1}]$$

$$= (-1)\cdot \frac{C_0V_0}{V_0+V} + (+5)\cdot \frac{CV}{V_0+V} \quad (17b)$$

$$Z_{Br}\cdot f_6 - (f_{12} + f_0 - f_3 - f_4 - 6\cdot f_5)$$

$$(Z_{Br}-5)(N_4+N_5) + (Z_{Br}-1)(N_6+N_7) + 2Z_{Br}N_8 + (3Z_{Br}+1)N_9 + (Z_{Br}+1)N_{10}$$

$$= (Z_{Br}+1)N_{01} + (Z_{Br}-5)N_{04} \quad \Rightarrow$$

$$(Z_{Br}-5)([HBrO_3]+[BrO_3^{-1}]) + (Z_{Br}-1)([HBrO]+[BrO^{-1}]) + 2Z_{Br}[Br_2] + (3Z_{Br}+1)[Br_3^{-1}] + (Z_{Br}+1)[Br^{-1}] \quad (18)$$

$$= (Z_{Br}+1)\cdot \frac{C_0V_0}{V_0+V} + (Z_{Br}-5)\cdot \frac{CV}{V_0+V} \quad (18a)$$

Other linear combinations are also possible. From the linear combination  $(f_{12} + f_0 - f_3 - f_4 - 6\cdot f_5 + f_6)/2$  we get the shortest (involving the smallest number of components) form of GEB for the system:

$$3(N_4+N_5) + (N_6+N_7) + N_8 + N_9 = 3N_{04} \quad \Rightarrow$$

$$3([HBrO_3] + [BrO_3^{-1}]) + ([HBrO] + [BrO^{-1}]) + [Br_2] + [Br_3^{-1}] = 3\cdot \frac{CV}{V_0+V} \quad (19)$$

Note that the coefficients in the linear combination (17) are equal to the oxidation numbers (ONs) of the elements: H, O, Na, K, S, considered as fans in the D+T system. Moreover, Eq. 17b obtained from the linear combination (17) interrelates components and species formed by Br, as the player.

Other linear combinations  $a_1\cdot f_0 + a_2\cdot f_{12} + \sum_{k=3}^6 a_k \cdot f_k$  of the balances:  $f_0, f_{12}, f_3, \dots, f_6$  are also possible, i.e. correct from mathematical viewpoint,  $a_k \in \mathbb{R}$ .

Equation 16 is the primary form of GEB,  $f_{12} = pr\text{-GEB}$ , for the D+T system. Equations: 17a,b, 18 and 19 are there alternative/equivalent equations for GEB, expressed in terms of concentrations. One of the equations for GEB (e.g. Eq. 19), together with equations: 11 - 15, form a complete set of equations related to this system. The relations 12 and 13, considered as equalities (not equations), can be immediately introduced into Eq. 11, like numbers.

In Eq. 14, the  $SO_4^{-2}$  can be perceived as the core. However, because this system has no other competing sulfate forms, the choice between the notations:  $f(S)$  and  $f(SO_4)$  is irrelevant.

One can notice that: (a)  $N_1$  – involved with  $H_2O$  as the species, (b)  $N_{03}$  and  $N_{05}$  – related to water as the component of the system, and (c) all  $n_i = n_{iW}$  ( $i=2, \dots, 14$ ) – specified in  $f(H)$  and  $f(O)$  are cancelled within  $f_{12} = 2\cdot f(O) - f(H)$  in aqueous media. The necessity of prior knowledge of  $n_{iW}$  values in the balancing procedure is thus avoided. All these regularities are valid for non-redox and redox systems.

### 3.1. Approach I to GEB in the System

Unlike the Approach II to GEB exemplified above, the Approach I to GEB needs prior knowledge of ONs for Br in all bromine components and species of the D+T system, where we have  $K^* = 5$  fans (H, O, K, Na, S) and  $K - K^* = 6 - 5 = 1$  player (Br).

In the D+T system, bromine (in NaBr and  $KBrO_3$ ) is the carrier/distributor of the player's electrons. One atom of Br has  $Z_{Br}$  bromine electrons. Therefore,  $N_{01}$  molecules of NaBr involve  $(Z_{Br}+1)\cdot N_{01}$  bromine electrons, and  $N_{04}$  molecules of  $KBrO_3$  involve  $(Z_{Br}-5)N_{04}$  bromine electrons. Thus, the total number of bromine electrons introduced by NaBr and  $KBrO_3$  is  $(Z_{Br}+1)\cdot N_{01} + (Z_{Br}-5)N_{04}$ . On this basis, we state that [3, 7, 11, 54]:

$N_4$ species $HBrO_3\cdot n_4H_2O$ involve	$(Z_{Br}-5)\cdot N_4$	bromine electrons;
$N_5$ species $BrO_3^{-1}\cdot n_5H_2O$ involve	$(Z_{Br}-5)\cdot N_5$	bromine electrons;
$N_6$ species $HBrO\cdot n_6H_2O$ involve	$(Z_{Br}-1)\cdot N_6$	bromine electrons;
$N_7$ species $BrO^{-1}\cdot n_7H_2O$ involve	$(Z_{Br}-1)\cdot N_7$	bromine electrons;
$N_8$ species $Br_2\cdot n_8H_2O$ involve	$2Z_{Br}\cdot N_8$	bromine electrons;
$N_9$ species $Br_3^{-1}\cdot n_9H_2O$ involve	$(3Z_{Br}+1)\cdot N_9$	bromine electrons;
$N_{10}$ species $Br^{-1}\cdot n_{10}H_2O$ involve	$(Z_{Br}+1)\cdot N_{10}$	bromine electrons.

The balance for the bromine electrons is then expressed by Eq. 18 and then by Eq. 18a. This confirms the equivalency of the Approaches I and II to GEB.

As stated above, the Approach I to GEB is compared to the 'card game' [3] (pp. 41-43), and – nominally – all electrons of the players are involved in the balance 18a. Following this line of reasoning, it can also be stated that the card players do not engage, as a rule, all their cash resources in the game. What's more – the 'debt of honour' principle can be applied [3] (p. 43). Simply, on the ground of linear combination, in Eq. 18a one can replace  $Z_{Br}$  for Br by  $\zeta_{Br} \neq Z_{Br}$  in Eq. 18a in particular, one can apply  $\zeta_{Br} = 0$ , see Eq. 17a in context with Eq. 18a.

### 3.2. Separate Subsystems: D = D(V<sub>0</sub>) and T = T(V)

For comparative purposes, we can formulate (Examples 1a, 1b) the balances for  $D = D(V_0)$  and  $T = T(V)$ , considered separately. The ONs for Br : -1 in D, and +5 in T are the boundary values of ONs in bromine redox systems [54].

### 3.3. The D = D(V<sub>0</sub>) Subsystem

Applying the notation specified above, we have:

$$f_0 = ChB : N_2 - N_3 - N_{10} + N_{11} - N_{13} - 2N_{14} = 0$$

$$f_1 = f(H) : 2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + 2N_{11}n_{11} + N_{13}(1+2n_{13}) + 2N_{14}n_{14} = 2N_{02} + 2N_{03}$$

$$\begin{aligned}
f_2 = f(\text{O}) : & \quad N_1 + N_2 n_2 + N_3(1+n_3) + N_{11} n_{11} + N_{13}(4+n_{13}) + N_{14}(4+n_{14}) = 4N_{02} + N_{03} \\
-f_3 = -f(\text{Na}) : & \quad N_{01} = N_{11} \\
-f_5 = -f(\text{SO}_4) : & \quad N_{02} = N_{13} + N_{14} \\
f_6 = f(\text{Br}) : & \quad N_{10} = N_{01} \\
\text{and then:} & \\
f_{12} = 2 \cdot f_2 - f_1 : & \quad -N_2 + N_3 + 7N_{13} + 8N_{14} = 6N_{02} \\
f_{12} + f_0 - f_3 - 6f_5 + f_6 = 0 \Leftrightarrow & \quad (+1)f(\text{H}) + (-2)f(\text{O}) + (+1)f(\text{Na}) + (+6)f(\text{S}) + \\
(-1)f(\text{Br}) - \text{ChB} = 0 & \quad (20) \\
0 = 0 & \quad (20a)
\end{aligned}$$

### 3.4. The T = T(V) Subsystem

$$\begin{aligned}
f_0 = \text{ChB} : & \quad N_2 - N_3 - N_5 + N_{12} = 0 \\
f_1 = f(\text{H}) : & \quad 2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5 n_5 + 2N_{12} n_{12} = 2N_{05} \\
f_2 = f(\text{O}) : & \quad N_1 + N_2 n_2 + N_3(1+n_3) + N_4(3+n_4) + N_5(3+n_5) + N_{12} n_{12} = 3N_{04} + N_{05} \\
-f_4 = -f(\text{K}) : & \quad N_{04} = N_{12} \\
-f_6 = -f(\text{Br}) : & \quad N_{04} = N_4 + N_5 \\
\text{and then:} & \\
f_{12} = 2 \cdot f_2 - f_1 : & \quad -N_2 + N_3 + 5N_4 + 6N_5 + 8N_{14} = 6N_{04} \\
f_{12} + f_0 - f_4 - 5f_6 = 0 \Leftrightarrow & \quad (+1)f(\text{H}) + (-2)f(\text{O}) + (+1)f(\text{K}) + (+5)f(\text{Br}) - \text{ChB} = 0 \quad (21) \\
0 = 0 & \quad (21a)
\end{aligned}$$

The relations  $0 = 0$ , named as identities (20a, 21a) [9, 29], mean here that:

- $f_{12}$  is linearly dependent on:  $f_0, f_3, f_5$  and  $f_6$  in Eq. 20, i.e.,  $f_{12} = f_3 + 6f_5 - f_6 - f_0$ ;
- $f_{12}$  is linearly dependent on:  $f_0, f_4$  and  $f_6$  in Eq. 21, i.e.,  $f_{12} = f_4 + 5f_6 - f_0$ .

In other words, the  $f_{12}$  are not the independent equations in  $D = D(V_0)$  and  $T = T(V)$ , considered consequently as separate non-redox subsystems.

### 3.5. Further Remarks

When formulating the balances  $f_1$  and  $f_2$ , it is possible to take into account the formation of water clusters  $(\text{H}_2\text{O})_\lambda$  ( $N_{1,\lambda}$ ,  $\lambda = 1, 2, \dots$ ) in aqueous solutions. Writing these balances as follows:

$$\begin{aligned}
f_1 = f(\text{H}) : & \\
2 \cdot \sum_{\lambda=1}^{\Lambda} \lambda \cdot N_{1,\lambda} + N_2(1+2n_2) + N_3(1+2n_3) + \dots & \\
f_2 = f(\text{O}) : & \\
\sum_{\lambda=1}^{\Lambda} \lambda \cdot N_{1,\lambda} + N_2(1+n_2) + N_3(1+n_3) + \dots &
\end{aligned}$$

we have:

$$\begin{aligned}
f_{12} = 2f_2 - f_1 : & \\
-N_2 + N_3 + \dots &
\end{aligned}$$

i.e., all components related to the clusters are cancelled.

### 3.6. Computer Program for the Redox System

```

function F = Function_NaBr_H2SO4_KBrO3(x)
%NaBr (C0) H2SO4 (C01) V0 <-- KBrO3 (C) V
global V Vmin Vstep Vmax V0 C C0 C01 fi H OH pH E Kw pKw A
global Br Br2 Br3 HBrO BrO HBrO3 BrO3 Na K HSO4 SO4
global logBr logBr2 logBr3 logHBrO logBrO logHBrO3 logBrO3
global logNa logK logHSO4 logSO4
E=x(1);
pH=x(2);
Br=10.^-x(3);
SO4=10.^-x(4);
H=10.^-pH;
pKw=14;
Kw=10.^-14;
OH=Kw./H;
A=16.9;
ZBr=35;
BrO3=Br.*10.^(6.*A.*(E-1.45)+6.*pH);
HBrO3=10.^0.7.*H.*BrO3;
BrO=Br.*10.^(2.*A.*(E-0.76)+2.*pH-2.*pKw);
HBrO=10.^8.6.*H.*BrO;
Br3=Br.^3.*10.^(2.*A.*(E-1.05));
Br2=Br.^2.*10.^(2.*A.*(E-1.087));
Na=C0.*V0./(V0+V);
K=C.*V./(V0+V);
%Charge balance

```



```

F=[(H-OH-BrO3-BrO-Br3-Br+Na+K-HSO4-2.*SO4);
%Concentration balance of Br
(HBrO3+BrO3+HBrO+BrO+2.*Br2+3.*Br3+Br-(C0.*V0.+C.*V)/(V0+V));
%Concentration balance for SO4
(HSO4+2.*SO4-C01.*V0/(V0+V));
%GEB
((ZBr-5).*(HBrO3+BrO3)+(ZBr-1).*(HBrO+BrO)+2.*ZBr.*Br2...
+(3.*ZBr+1).*Br3+(ZBr+1).*Br...
-((ZBr+1).*C0.*V0+(ZBr-5).*C.*V)/(V0+V));
logBr=log10(Br);
logBr2=log10(Br2);
logBr3=log10(Br3);
logHBrO=log10(HBrO);
logBrO=log10(BrO);
logHBrO3=log10(HBrO3);
logBrO3=log10(BrO3);
logHSO4=log10(HSO4);
logSO4=log10(SO4);
logNa=log10(Na);
logK=log10(K);

```

Equations: 9 - 13 and 16 are included in the minimized function F. All relations for equilibrium constants in the system tested [41, 50] are also specified here. In the algorithm, prepared according to MATLAB computational software [2], the potential E [V] is expressed in SHE scale;  $\text{pH} = -\log[\text{H}^+]$ ,  $\text{pBr} = -\log[\text{Br}^-]$ .

#### 4. Graphical Presentation of Results for the D+T System and Discussion

Results of calculations, presented graphically in Figure 1, were obtained at  $V_0 = 100$ ,  $C_0 = 0.01$ ,  $C = 0.1$  and different  $C_{01}$  [mol/L] values indicated at the graphs: (a)  $E = E(\Phi)$ , (b)  $\text{pH} = \text{pH}(\Phi)$  and (c) speciation curves  $\log[X_i^{z_i}] = \varphi_i(\Phi)$ , with the fraction titrated  $\Phi$  (Eq. 10) on the abscissas. The impact of growth in  $C_{01}$  concentration is presented there.

At  $C_{01} = 0$ , symproportionation practically does not occur (Fig. 1c); concentration of HBrO, as the major product formed in the reaction 9c is ca.  $10^{-6}$  mol/L. The potential E increases monotonically (Fig. 1a), whereas pH first increases, passes through maximum and then decreases (Fig. 1b). The relevant E and pH changes are small (Fig. 1a,b). Binding the  $\text{H}^+$  ions in reaction 9c causes a weakly alkaline reaction (Fig. 1b).

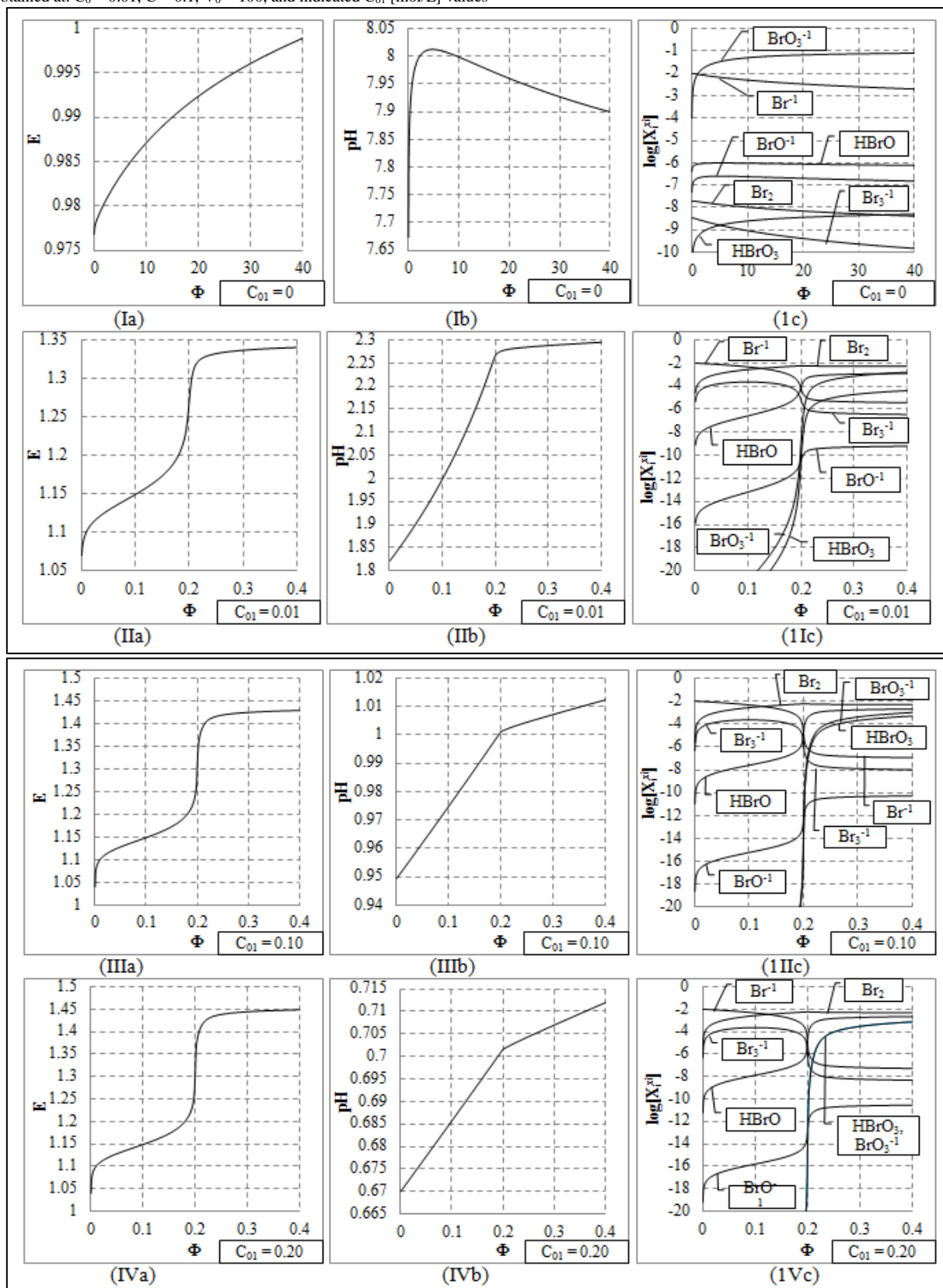
At  $C_{01} > 0$ , the stoichiometry 1 : 5, i.e.,  $\Phi_{\text{eq}} = 0.2$  (see [27, 54], resulting from the shape of the related graphs in Figures 1Ia,b, 1IIa,b, 1IVa,b, is expressed by Eq. 9a. For  $\Phi > 0.2$ , the effect of reactions 9a,b is also significant.

A growth of  $C_{01}$  value causes a small extension of the potential range in the jump region, on the side of higher E-values (Fig. 1a - 1IVa). With an increase of the  $C_{01}$  value, the graphs of pH vs.  $\Phi$  resemble two almost straight line segments intersecting at  $\Phi_{\text{eq}} = 0.2$  (Fig. 1b - 1IVb). However, the pH-ranges covered by the titration curves are gradually narrowed; it results from growth of dynamic buffer capacity [30] in the related redox systems.

#### 5. Concluding Remarks

- Starting from  $K+1$  balances:  $f_0, f_1, f_2, f_3, \dots, f_K$ , after formulation of the linear combination  $f_{12}$  we obtain the set of  $K$  balances:  $f_0, f_{12}, f_3, \dots, f_K$ .
- The proper linear combination of  $f_k$  for fans, with coefficients  $d_k$  equal to ONs (see Eq. 17), is the way towards the simplest/shortest form of GEB; the shortest form (Eq. 19a) was obtained here after further combination with the balance for Br (player). For a non-redox system, the linear combination of  $f_0$  with  $f_k$  for fans is the way towards identity  $0 = 0$ .
- In a non-redox system,  $f_{12}$  is the dependent balance; we have there  $K-1$  independent balances:  $f_0, f_3, \dots, f_K$ . In other words,  $f_{12}$  is not an independent balance in a non-redox system; it is therefore omitted in formulation of any non-redox system. The identity  $0 = 0$  for the proper linear combination indicates that the equations  $f_0, f_{12}, f_3, \dots, f_K$  are linearly dependent for non-redox systems.
- In a redox system,  $f_{12}$  is the independent balance; then we have  $K$  independent balances:  $f_0, f_{12}, f_3, \dots, f_K$ , involved with GEB, ChB, and elemental/core balances  $f(Y_k)$  ( $k=3, \dots, K$ ), respectively..
- The number of elemental/core balances,  $f_3, \dots, f_K$ , equals  $K-2$ , both in non-redox and redox systems.
- The linear independency/dependency of  $f_{12} = 2 \cdot f(\text{O}) - f(\text{H})$  from other balances:  $f_0, f_3, \dots, f_K$  is the general criterion distinguishing between redox and non-redox systems;
- The  $f_{12}$  is the primary form of Generalized electron balance (GEB),  $f_{12} = pr\text{-GEB}$ , completing the set of  $K$  balances  $f_0, f_{12}, f_3, \dots, f_K$  necessary for solution of redox systems, of any degree of complexity.
- Any linear combination of  $f_{12}$  with the balances  $f_0, f_3, \dots, f_K$  has full properties of GEB related to the redox system considered, i.e., all them are equivalent forms of GEB.

**Figure-1.** Plots for the D+T system:  $E = E(\Phi)$  – column (a),  $pH = pH(\Phi)$  – column (b) and speciation diagrams  $\log[X_i^{z_i}] = \phi_i(\Phi)$  – column (c), obtained at:  $C_0 = 0.01$ ,  $C = 0.1$ ,  $V_0 = 100$ , and indicated  $C_{01}$  [mol/L] values



- The Approach II to GEB does not indicate oxidants and reductants, i.e., oxidized and reduced forms of the redox system in question.
- The prior knowledge of oxidation numbers (ONs) for all elements of the system is not required within the formalism scheme realized according to Approach II; this fact is of capital importance for the systems where redox equilibria are involved, e.g., with complex organic species; the known composition of a species, expressed by its formula, together with external charge of this species, provides information sufficient to formulate the related balances.

- When the oxidation numbers of all elements of a system are known beforehand, the GEB can be formulated according to Approach I to GEB, known also as the 'short version' of GEB; the GEB obtained according to Approach I to GEB involves all electron-active elements – as components and species – of the system tested.
- Both Approaches (I and II) to GEB are equivalent.
- The criterion distinguishing between non-redox and redox systems equivalence is valid for electrolytic systems of any degree of complexity. It was also confirmed for electrolytic systems in binary and (generally) mixed-solvent  $A_s$  ( $s=1,\dots,S$ ) media [10, 55, 56], where mixed solvates  $X_i^{z_i} \cdot n_{iA_1} \dots n_{iA_s} \dots n_{iA_S}$  are assumed, and  $n_{iA_s} \geq 0$  is the mean numbers of  $A_s$  molecules attached to  $X_i^{z_i}$ .
- The formulation of GEB according to Approach II is relatively/extraordinarily simple, although receiving the shorter equation for GEB, when using the linear combinations of *pr*-GEB with other balances, requires implementation of the time-consuming, preparatory activities. However, the formulation of GEB according to Approach II has – undoubtedly – the cognitive advantages, even in the cases when the oxidation numbers for all elements in the system are known beforehand.

## 6. Final Comments

The GEB concept is perceived as the law of the matter conservation, as the general law of Nature [3], as the hidden connection of physicochemical laws, and as a breakthrough in thermodynamic theory of electrolytic redox systems. The GATES/GEB is an example of excellent paradigm, as the best possible thermodynamic approach to electrolytic redox systems. Other/earlier approaches to formulation of electrolytic redox systems, based on stoichiometric principles, were unsuccessful, for obvious reasons. All them were thoroughly criticized in our review papers [1, 6, 7, 25, 38, 46], and elsewhere.

The Approach II to GEB does not require any prior knowledge of the oxidation numbers of elements in the components and 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 [57]. In GATES formulation, it results naturally from the linear combination; within the Approach II to GEB, ON is then the derivative concept. 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.

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 ([25], pp. 361-363) of free electrons 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 and non-aqueous media, with amphiprotic (co)solvents involved.

## 7. Epilogue

We can also express/repeat our conviction [6] that the Approach II to GEB in context with GATES will lead to gradual elimination of the stoichiometry concept from the quantitative (not qualitative/descriptive) consciousness of chemists (see the picture below).



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