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Research Article

The Balance 2·f (O) – f (H) as a Cornerstone in Formulation of Electrolytic Systems

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Abstract

The Generalized Electron Balance (GEB) concept, related to electrolytic redox systems, is considered according to principles of Generalized Approach to Electrolytic Systems (GATES). Two equivalent Approaches (I and II) to GEB are presented. The Approach I, when perceived in convention of the card game, is 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. The GEB obtained according to Approach II results from 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. Very important properties of f_{12} are presented here in detail, and illustrated by a redox system where comproportionation reactions occur.

Keywords:
Thermodynamics; Electrolytic systems; Redox titrations; Oxidation numbers

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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, can be formulated for electrolytic redox and non-redox systems, of any degree of complexity, where charge ($f_0 = ChB$) and elemental/core balances $f_k = f(Y_k)$for $Y_k \neq H, O$ ($k \geq 3, \ldots, K$) are also formulated, according to Generalized approach to redox systems (GATES) principles. The set of K independent balances $f_0, f_{12}, f_3, \ldots, f_K$ is necessary for thermodynamic resolution of a redox system; all the balances are presented here in the form $f_k = 0$ ($k = 0, \ldots, K$). A non-redox system is resolvable with use of K–1 independent balances $f_0, f_3, \ldots, f_K$. In a non-redox system, f_{12} is the dependent balance, indicated by the linear combination $LC = \sum_{k=1}^{K} d_k \cdot f_k - f_0$, where d_k are the oxidation numbers (ONs) for $Y_1 = H$, $Y_2 = O$, and Y_k ($k \geq 3, \ldots, K$). For a non-redox system, the LC is expressed by identity, $0 = 0$, i.e., f_{12} is linearly dependent on $f_0, f_3, \ldots, f_K$, and then $f_{12} = \sum_{k=3}^{K} d_k \cdot f_k - f_0$. For a redox system, LC is expressed by equation different from the identity, i.e., f_{12} is the new balance in the redox system. Therefore, the linear dependency/independency of f_{12} from $f_0, f_3, \ldots, f_K$ is the general criterion distinguishing between non-redox and redox systems, of any degree of complexity.

The Approach II to GEB (formulated 2005) was preceded by the Approach I to GEB (formulated 1992); both approaches are equivalent, i.e.,

$$\text{Approach I to GEB} \Longleftrightarrow \text{Approach II to GEB} \quad \textbf{(1)}$$

Formulation of GEB according to Approach I can be perceived in the convention of the 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. In a redox system, the arranged set ($f_1, f_2, \ldots, f_{k^*}, f_{k^*+1}, \ldots, f_K$) of K balances $f_1, \ldots, f_K$ involves K^* balances $f_1, f_2, \ldots, f_{k^*}$, for fans, and $K - K^*$ balances $f_{k^*+1}, \ldots, f_K$ for players. In a non-redox system we have $K^* = K$ fans, i.e., the number of players is $K - K^* = 0$ in there; H and O are considered here as fans.

The prior knowledge of ONs for all elements of the system in question is not needed in the Approach II to GEB, contrary to the formulation of GEB according to Approach I, where the knowledge of ONs for players is required.

All the regularities indicated above will be confirmed in an example presented below, and illustrated graphically. Further generalizing comments will also be presented.

Redox Systems in Chemistry

In chemical laboratories, redox reactions are usually referred to processes occurred during redox titrations. Since redox reactions are so important a class of chemical reactions, we should know their physicochemical nature thoroughly, from the titrimetric viewpoint.

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 obtained, if the volume additivity is valid/tolerable. The species formed in the D+T systems are involved in the related balances.

In aqueous media, the species $X_i^{z_i}$ exist as hydrates $X_i^{z_i} \cdot n_{iW}$; $z_i = 0, \pm 1, \pm 2, \ldots$ is a charge, expressed in terms of elementary charge units, $e = F/N_A$ ($F = 96485$ C·mol^{-1} – Faraday's constant, $N_A = 6.022 \cdot 10^{23}$ mol^{-1} – Avogadro's number), $n_i = n_{iW} \geq 0$ is a mean number of water ($W=H_2O$) molecules attached to $X_i^{z_i}$; the case $n_{iW} = 0$ is then also admitted. For ordering purposes we assume: $X_2^{z_2} \cdot n_{i2W} = H^{+1} \cdot n_{2W}$, $X_3^{z_3} \cdot n_{3W} = OH^{-1} \cdot n_{3W}$, i.e., $z_2 = +1$, $z_3 = -1$, … . Molar concentration of the species $X_i^{z_i} \cdot n_{iW}$is denoted as $\left[X_i^{z_i}\right]$; for a static system (volume V_0 mL), we have

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

and for a dynamic D+T system

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

It is advisable to start the balancing from the interrelations between numbers of particular entities: N_{0j} for components represented by molecules composing D and T, and N_i – for species $X_i^{z_i} \cdot n_{iW}$ (ions and molecules) of i-th kind (i = 1, …, I), where I is the number of kinds of the species in the D+T. The mono- or two-phase electrolytic D+T system thus obtained involves N_1 molecules of H_2O and N_i species of i-th kind, $X_i^{z_i} \cdot n_{iW}$ (i = 2, 3, …, I), specified briefly as $X_i^{z_i}$ (N_i, n_i), where $n_i \equiv n_{iW} \equiv n_iH_2O$ is the mean number of hydrating water molecules (W=H_2O) attached to $X_i^{z_i}$. The net charge of $X_i^{z_i} \cdot n_{iW}$ equals to the charge of $X_i^{z_i}$: $z_i + n_{iW} \cdot 0 = z_i$. For ordering purposes, we write the sequence: H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3), … , i.e., $z_2 = 1$, $z_3 = -1$.

In the notation applied here, N_{0j} (j =1, 2, …, J) is the number of molecules of the component of j-th kind, including water, forming D in static (V=0), or D and T in a dynamic D+T system. The D+T system thus obtained involves N_1 molecules of H_2O ($X_i^{z_i} = H_2O$, $z_1=0$) and N_i species of i-th kind, (i = 2, 3, …, I), denoted briefly as $X_i^{z_i} \cdot n_{iW}$, where $n_i \equiv n_{iW} \equiv n_iH_2O$. The $n_i = n_{iW}$ values are virtually unknown – even for $X_i^{z_i} = H^{+1}$ [1] in aqueous media, and depend on ionic strength (I) of the solution.

Electrolytic (redox and non-redox) systems are formulated according to the GATES principles [2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20], [21], [22], [23], [24], [25], [26], [27], [28], [29], [30], [31], [32], [33], [34], [35], [36], [37], [38], [39], [40]. For this purpose, the set of K+1 balances f_0, f_1, f_2, f_3, …, f_K is obtained. The charged/ionic species of the system are involved in the charge balance

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

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

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., $0 \cdot [H_2O] = 0$ (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(H) and f_2 = f(O):

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

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

Next, the linear combination

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

is obtained, where a_{ki} and b_{kj} in equations 4-6 are the numbers of atoms/cores Y_k (k = 1,...,K) in $X_i^{z_i} \cdot n_{iW}$, and in the j-th component of the system, resp. The core is perceived as a non-transformable cluster of atoms, of the same elemental composition (expressed by chemical formula) and structure; e.g. the set of species: HSO_4^{-1}, SO_4^{-2} and $FeSO_4$ contains SO_4^{-2} as the core. One can notice that:

(a)

N_1 involved with H_2O as the species,

(b)

all N_{0i} related to water as the component of the system, and

(c)

all $n_i = n_{iW}$ specified in f(H) and f(O) are cancelled within 2·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.

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

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

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

In further parts of this paper, we are concerned with the procedure known in elementary algebra as linear combination [19], [41], in accordance with Noether's conceptual approach to linear algebra [42], [43]. For this purpose, we consider first an example of titration in a redox system, where comproportionation [44] reactions occur. The conclusions arising in the formulation of this system (denoted as the system S, for brevity) will then be generalized later in the discussion.

System S: $KBrO_3$ (C) ⇒NaBr (C_0) + H_2SO_4 (C_{01})

Let us consider the system, where V_0 mL of D is composed of NaBr (N_{01} molecules) + H_2SO_4 (N_{02} molecules) + H_2O (N_{03} molecules), and V mL of T is composed of $KBrO_3$ (N_{04} molecules) + H_2O (N_{05} molecules). The D+T mixture thus formed involves the following species:

H_2O (N_1), H^{+1} (N_2,n_2), OH^{-1} (N_3,n_3), $HBrO_3$ (N_4,n_4), BrO_3^{-1} (N_5,n_5), HBrO (N_6,n_6), BrO^{-1} (N_7,n_7),

Br_2 (N_8,n_8), Br_3^{-1} (N_9,n_9), Br^{-1} (N_{10},n_{10}), Na^{+1} (N_{11},n_{11}) , K^{+1} (N_{12},n_{12}),

HSO_4^{-1} (N_{13},n_{13}), SO_4^{-2} (N_{14},n_{14}).

The Approach II to the System S

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 [16], [25], [45]

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \tag{8}$$

It provides a kind of normalization in the related graphs, i.e., independency on V_0 value. The balances are as follows:

f_0 = ChB :

$$N_2 - N_3 - N_5 - N_7 - N_9 - N_{10} + N_{11} + N_{12} - N_{13} - 2N_{14} = 0 \Longrightarrow \tag{9}$$

$$[H^{+1}] - [OH^{-1}] - [BrO_3^{-1}] - [BrO^{-1}] - [Br_3^{-1}] - [Br^{-1}] + [Na^{+1}] + [K^{+1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] = 0 \tag{9a}$$

$f_1 = f(H)$:

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

$f_2 = f(O)$:

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

$-f_3 = -f(Na)$:

$$N_{01} = N_{11} \Longrightarrow [Na^{+1}] = C_0V_0/(V_0+V) \quad (10)$$

$-f_4 = -f(K)$:

$$N_{04} = N_{12} \Longrightarrow [K^{+1}] = CV/(V_0+V) \quad (11)$$

$$-f_5 = -f(SO_4) \Longleftrightarrow -f_5 = -f(S): \quad (12)$$

$$N_{02} = N_{13} + N_{14} \Longrightarrow \quad (12a)$$

$$[HSO_4^{-1}] + [SO_4^{-2}] = C_{01}V_0/(V_0+V) \quad (12b)$$

$$f_6 = f(Br) : N_4 + N_5 + N_6 + N_7 + 2N_8 + 3N_9 + N_{10} = N_{01} + N_{04} \Longrightarrow \quad (13)$$

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

$$f_{12} = 2\,f(O) - f(H) - N_2 + N_3 + 5N_4 + 6N_5 + N_6 + 2N_7 + 7N_{13} + 8N_{14} = 6N_{02} + 6N_{04} \quad (14)$$

$$-[H^{+1}] + [OH^{-1}] + 5[HBrO_3] + 6[BrO_3^{-1}] + [HBrO] + 2[BrO^{-1}] + 7[HSO_4^{-1}] + 8[SO_4^{-2}] = 6(C_{01}V_0 + CV)/(V_0+V) \quad (14a)$$

$$f_{12} + f_0 - f_3 - f_4 - 6\cdot f_5 = 0 \Longleftrightarrow (+1)f_1 + (-2)f_2 + (+1)f_3 + (+1)f_4 + (+6)f_5 - f_0 = 0 \Longleftrightarrow (+1)f(H) + (-2)f(O) + (+1)f(Na) + (+1)f(K) + (+6)f(S) - ChB = 0 \quad (15)$$

$$5(N_4+N_5) + 1(N_6+N_7) - N_9 - N_{10} = -N_{01} + 5N_{04} \Longrightarrow \quad (15a)$$

$$5([HBrO_3] + [BrO_3^{-1}]) + [HBrO] + [BrO^{-1}] - [Br_3^{-1}] - [Br^{-1}] = -\frac{C_0V_0}{V_0+V} + 5\cdot\frac{CV}{V_0+V} \quad (15b)$$

$$(+5)([HBrO_3]+[BrO_3^{-1}]) + (+1)([HBrO]+[BrO^{-1}]) + 2\cdot 0\cdot[Br_2] + 3\cdot\left(-\frac{1}{3}\right)\cdot[Br_3^{-1}] + (-1)[Br^{-1}] = (-1)\cdot\cdot\frac{C_0V_0}{V_0+V} + (+5)\cdot\cdot\frac{CV}{V_0+V} \quad (15c)$$

$$Z_{Br}\cdot f_6 - (f_{12} + f_0 - f_3 - f_4 - 6\cdot f_5)$$
$$(Z_{Br}-5)(N_4+N_5) + (Z_{Br}-1)(N_6+N_7) + 2Z_{Br}N_8 + (3Z_{Br}+1)N_9 + (Z_{Br}+1)N_{10} = (Z_{Br}+1)N_{01} + (Z_{Br}-5)N_{04} \Longrightarrow \quad (16)$$

$$(Z_{Br}-5)([HBrO_3]+[BrO_3^{-1}]) + (Z_{Br}-1)([HBrO]+[BrO^{-1}]) + 2Z_{Br}[Br_2] + (3Z_{Br}+1)[Br_3^{-1}] + (Z_{Br}+1)[Br^{-1}] = (Z_{Br}+1)\cdot\frac{C_0V_0}{V_0+V} + (Z_{Br}-5)\cdot\frac{CV}{V_0+V} \quad (16a)$$

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 S:

$$3(N_4+N_5) + (N_6+N_7) + N_8 + N_9 = 3N_{04} \quad (17)$$

$$3([HBrO_3] + [BrO_3^{-1}]) + ([HBrO] + [BrO^{-1}]) + [Br_2] + [Br_3^{-1}] = 3\cdot\frac{CV}{V_0 + V} \quad \textbf{(17a)}$$

Note that the coefficients in eq. 15c are equal to the oxidation numbers (ONs) of the elements considered as 'fans' in the system S, i.e., H, O, Na, K, S. Eq. 15b obtained from the combination 15 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, …, f_6 are also acceptable, $a_k \in \mathbb{R}$.

Equations 14a, 15b, 16a and 17a are alternative/equivalent equations for GEB related to the system S. One of the equations for GEB, together with equations 9a, 12b and 13a, forms a complete set of equations related to the system S. The relations 10 and 11, considered as equalities (not equations), can be immediately introduced into eq. 9a as numbers.

In eq. 12b, the SO_4^{-2} can be perceived as the core. However, because the system S has no other competing sulfate forms, the choice between f(S) and f(SO_4) (eq. 12) is irrelevant.

Separate Approaches to D and T of the System S

We can also formulate the balances for D and T, considered separately, as independent units. Applying the notation specified above, we have:

for D:

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

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

$$f_2 = f(O) : N_1 + N_2n_2 + N_3(1+n_3) + N_{11}n_{11} + N_{13}(4+n_{13}) + N_{14}(4+n_{14}) = 4N_{02} + N_{03}$$

$-f_3 = -f(Na) : N_{01} = N_{11}$

$-f_5 = -f(SO_4) : N_{02} = N_{13} + N_{14}$

$f_6 = f(Br) : N_{10} = N_{01}$

and then:

$f_{12} = 2\cdot f_2 - f_1 : -N_2 + N_3 + 7N_{13} + 8N_{14} = 6N_{02}$

$$f_{12} + f_0 - f_3 - 6f_5 + f_6 = 0 \Longleftrightarrow (+1)f(H) + (-2)f(O) + (+1)f(Na) + (+6)f(S) + (-1)f(Br) - ChB = 0 \quad \textbf{(18)}$$

$$0 = 0 \quad \textbf{(18a)}$$

for T:

$f_0 = ChB : N_2 - N_3 - N_5 + N_{12} = 0$

$$f_1 = f(H) : 2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + 2N_{12}n_{12} = 2N_{05}$$

$$f_2 = f(O) : N_1 + N_2n_2 + N_3(1+n_3) + N_4(3+n_4) + N_5(3+n_5) + N_{12}n_{12} = 3N_{04} + N_{05}$$

$-f_4 = -f(K) : N_{04} = N_{12}$

$-f_6 = -f(Br) : N_{04} = N_4 + N_5$

and then:

$f_{12} = 2\cdot f_2 - f_1 : -N_2 + N_3 + 5N_4 + 6N_5 + 8N_{14} = 6N_{04}$

$$f_{12} + f_0 - f_4 - 5f_6 = 0 \Longleftrightarrow (+1)f(H) + (-2)f(O) + (+1)f(K) + (+5)f(Br) - ChB = 0 \quad \textbf{(19)}$$

$$0 = 0 \quad \textbf{(19a)}$$

The D and T, considered separately, form non-redox-systems; ONs for Br are: –1 in NaBr, and +5 in $KBrO_3$, i.e., there are the boundary values of ONs in bromine redox systems; Br(+7) species are omitted in considerations [24].

The relations 0 = 0, named as identities, mean here that:

f_{12} is linearly dependent on: f_0, f_3, f_5 and f_6 in eq. 18, 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. 19, i.e., $f_{12} = f_4 + 5f_6 – f_0$.

In other words, the f_{12} are not the independent equations in D and T, considered here as separate subsystems.

Approach I to GEB in the System S

Unlike the Approach II exemplified above, the Approach I to GEB needs prior knowledge of ONs for all elements in components and species of the system in question. In the system S, there are $K^* = 5$ 'fans', whereas bromine (Br) is considered as the 'player, $K – K^* = 6 – 5 = 1$ is here the number of players.

In the system S, bromine (as NaBr and $KBrO_3$) is the carrier/distributor of the player electrons. One atom of Br has Z_{Br} bromine electrons, and then one molecule of NaBr has Z_{Br} +1 bromine electrons, one molecule of $KBrO_3$ has Z_{Br}–5 bromine electrons; then N_{01} molecules of NaBr involve $(Z_{Br} + 1)\cdot N_{01}$ bromine electrons, 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 [2], [27]:

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. 16 and then by eq. 16a. This confirms the equivalency of the Approaches I and II to GEB (eq. 1).

As stated above, the Approach I to GEB is compared to the 'card game' [27] (pp. 41-43), and – nominally – all electrons of the players are involved in the balance 16a. Following this line of reasoning, it can be also 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 [27] (p. 43). Simply, on the ground of linear combination, in eq. 16a one can replace Z_{Br} for Br by $\zeta_{Br} \neq Z_{Br}$; in particular, one can apply $\zeta_{Br} = 0$, see equations 15a and 15b in context with equations 16 and 16a.

Computer Program for the System S

```
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
```

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```
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);
```

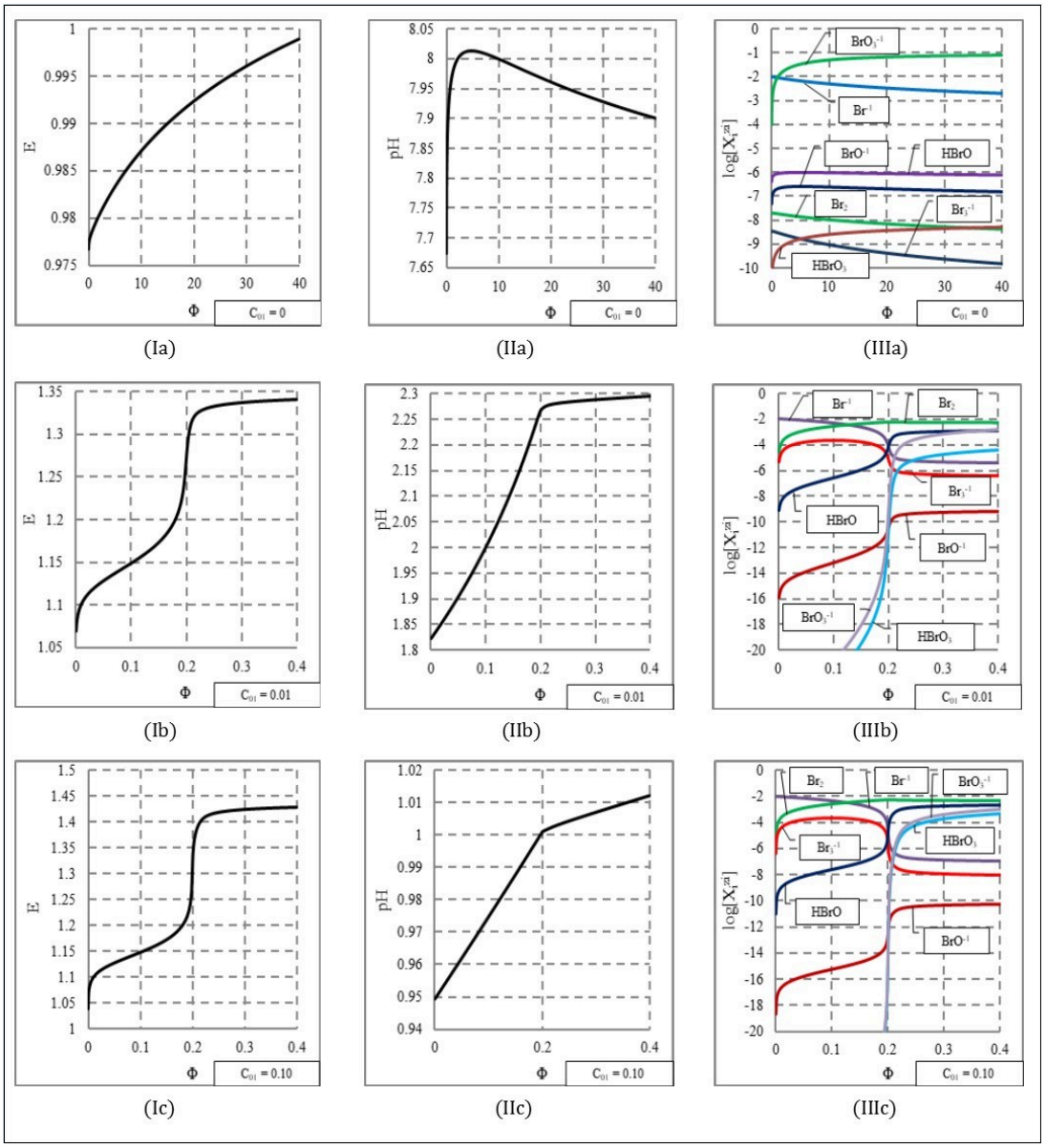


Figure 1. The functions: E = E(Φ) (column I), pH = pH(Φ) (column II) and speciation diagrams (column III), at (C_0,V_0,C) = (0.01,100,0.1), and three different C_{01} values, indicated at the graphs.

Graphical Presentation of Results for the System S

In the algorithm, prepared according to MATLAB computational software, the potential E^V was expressed in SHE scale [46], pH = – log[H^{+1}], pBr = – log[Br^{-1}], V_0 = 100, C_0 = 0.01, C = 0.1, C_{01} = 0, 0.01 or 0.1. The equilibrium constants related to this system were cited in ref. [2].

The results of calculations are presented graphically (Figure 1), as the graphs: (a) E = E(Φ), (b) pH = pH(Φ) and (c) speciation curves [X_i^{Zi}] = φ_i(Φ), with the fraction titrated Φ (eq. 8) on the abscissas. The impact of growth in C_{01} concentration is illustrated here.

At C_{01} = 0, comproportionation practically does not occur (IIIa); concentration of HBrO, as the major product formed in the comproportionation reaction

$$BrO_3^{-1} + 2Br^{-1} + 3H^{+1} = 3HBrO \quad \textbf{(20)}$$

is ca. 10^{-6} mol/L. The potential E increases monotonically (Figure Ia), whereas pH first increases, passes through a maximum and then decreases, see IIa). The relevant E and pH changes are small (Figures Ia, IIa). Binding the H^{+1} ions in reaction 21 causes a weakly alkaline reaction (Figure IIa).

At C_{01} = 0.01 (Figures Ib, IIb, IIIb) and 0.1 (Figures Ic, IIc, IIIc), the stoichiometry 1: 5, i.e., Φ_{eq} = 0.2, see [16], [28], resulting from the shape of the related graphs, is expressed by reaction

$$BrO_3^{-1} + 5Br^{-1} + 6H^{+1} = 3Br_2 + 3H_2O \quad \textbf{(21)}$$

For $\Phi > 0.2$, an increase of efficiency of the competing reaction 21 is noted. 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 (Figure 1, column I). With an increase of the C_{01} value, the graphs of pH vs. Φ resemble two almost straight line segments intersecting at Φ_{eq} = 0.2 (Figure 2, column II). However, the pH-ranges covered by the titration curves are gradually narrowed; it is an effect in growth of dynamic buffer capacity of the related redox systems [32].

Concluding remarks

The linear combination

$$\begin{gathered} f_0 + f_{12} - \sum_{k=3}^{K} d_k \cdot f_k = 0 \Longleftrightarrow \\ \sum_{k=3}^{K} d_k \cdot f_k - (f_{12} + f_0) = 0 \Longleftrightarrow \\ f_1 - 2 \cdot f_2 + \sum_{k=3}^{K} d_k \cdot f_k - f_0 = 0 \Longleftrightarrow \\ \sum_{k=1}^{K} d_k \cdot f_k - f_0 = 0 \end{gathered} \quad \textbf{(22)}$$

involves K balances: f_0, f_{12}, f_3,…,f_K where d_1 = +1, d_2 = –2. All the balances are presented here as equations, $f_k = 0$.

In a non-redox system, we have K fans, i.e., the number of players equals zero. In a redox system, we have K^* fans, $K^* < K$, i.e., the number of players equals $K - K^*$ (> 0).

When the multipliers d_k are equal to (or involved with) the oxidation numbers (ONs) of the corresponding elements (k = 1, …, K) in a non-redox system, then eq. 22 is transformed into identity, 0 = 0. This proves that f_{12} is not the independent equation in the f_0, f_{12}, f_3, …, f_K, and $f_{12} = \sum_{k=3}^{K} d_k \cdot f_k - f_0$. Then f_0, f_3, …, f_K is the set of K–1 independent balances, composed of charge balance (f_0) and K–2 elemental/core balances f_3, …, f_K.

Referring now to a redox system, we arrange the elemental/core balances in the sequence f_1, f_2, …, f_{K^*}, f_{K^*+1}, f_K, and then formulate the equation

$$\sum_{k=1}^{K^*} d_k \cdot f_k - f_0 = 0 \quad \textbf{(23)}$$

involving the balances for K^* electron-non-active elements, compare with equations 15, 18, 19.

If d_k (k=1,…,K^*) are equal to (or involved with) ONs of electron-non-active elements, then the resulting balance involves only the components (N_i, N_{0j}) related to electron-active species/compounds, with coefficients equal to (or involved with) ONs of these elements. More precisely, d_k are the products of the number λ_k of defined atoms in the species and the ON value ω_k, i.e. $d_k = \lambda_k \cdot \omega_k$ (k = 1,…,K^*). It is clearly visible in the case of Br_3^{-1} in eq. 15c, where $-1 = 3 \cdot \left(-\frac{1}{3}\right)$, and (less visible) in the case of Br_2 in the eq. 15c, where $0 = 2 \cdot 0$, i.e., the coefficient $d_9 = -1$ at $[Br_3^{-1}]$ in eq. 15b is involved with (not equal to) the oxidation number $\omega_9 = \left(-\frac{1}{3}\right)$ of bromine in Br_3^{-1} ($\lambda_9 = 3$).

The equivalent relations were applied:

$$\begin{gathered} f_k = \sum_{i=1}^{I} a_{ki} \cdot N_i - \sum_{j=1}^{J} b_{kj} \cdot N_{0j} = 0 \Longleftrightarrow \\ \sum_{i=1}^{I} a_{ki} \cdot N_i = \sum_{j=1}^{J} b_{kj} \cdot N_{0j} \end{gathered} \quad \textbf{(24)}$$

for elements with negative oxidation numbers, or

$$\begin{gathered} -f_k = \sum_{j=1}^{J} b_{kj} \cdot N_{0j} - \sum_{i=1}^{I} a_{ki} \cdot N_i = 0 \Longleftrightarrow \\ \sum_{j=1}^{J} b_{kj} \cdot N_{0j} = \sum_{i=1}^{I} a_{ki} \cdot N_i \end{gathered} \quad \textbf{(25)}$$

for elements with positive oxidation numbers, k ∈ 3, …,K. The change of places of numbers N_i for components and N_{0j} for species at the equality sign in relations 24, 25 were made in order to avoid possible/simple mistakes in the realization of the linear combination procedure. This facilitates the purposeful linear combination of the balances, and enables to avoid simple mistakes in this operation. Note, for example, that $f_4 = f(Na) \Longleftrightarrow f(Na) = f_4 \Longleftrightarrow -f_4 = -f(Na)$.

Starting from K+1 balances: f_0, f_1, f_2, f_3, …, f_K,, after formulation of the linear combination f_{12} we obtain the set of K balances: f_0, f_{12}, f_3, …, f_K,. In a non-redox system, f_{12} is the dependent balance; we have there K–1 independent balances: f_0, f_3, …, f_K. In other words, f_{12} is not a new, independent balance in non-redox systems; it is then omitted in formulation of any non-redox system. The identity 0 = 0 for the linear combinations indicates that the equations f_0, f_{12}, f_3, …, f_K, are linearly dependent for non-redox systems. In a redox system, f_{12} is the independent balance (i.e., different from the identity, 0=0); then we have K independent balances: f_0, f_{12}, f_3, …, f_K, that will be rearranged – optionally – as the set (f_{12}, f_0, f_3, …, f_K) involved with GEB, ChB, and $f(Y_k)$ (k = 3, …, K), respectively. The number of elemental/core balances, both in non-redox and redox systems, equals K–2. Then:

• For a non-redox system, a proper linear combination of f_{12} with f_0, f_3, …, f_K is reducible to identity 0 = 0, i.e., f_{12} is linearly dependent on f_0, f_3, … , f_K (equations 24,25).

• For a redox system, any linear combination of f_{12} with f_0, f_3, …, f_K is not reducible to identity 0 = 0, i.e., f_{12} is linearly independent of f_0, f_3, …, f_K.

• In conclusion, the linear independency/dependency of $f_{12} = 2 \cdot f(O) - f(H)$ from other balances: f_0, f_3, …, f_K is the general criterion distinguishing between redox and non-redox systems; the proper linear combination LC with d_k equal to ON's (see eq. 15), is the way towards the simplest/shortest form of GEB; the shortest form (eq. 17a) was obtained after further combination with the balance for Br (player). For a non-redox system, the linear combination indicated it is the way towards identity 0 = 0 (equations 18a, 19a).

• $f_{12} = 2 \cdot f(O) - f(H)$ is the primary form of Generalized Electron Balance (GEB), f_{12} = prGEB, completing the set of K balances f_0, f_{12}, f_3, …, f_K necessary for resolution of redox systems of any degree of complexity.

• Any linear combination of f_{12} with the balances f_0, f_3, …, f_K has full properties of GEB related to the redox system considered, i.e., all of them are equivalent forms of GEB.

• The Approach II to GEB does not indicate oxidants and reductants, i.e., oxidized and reduced forms in the system in question.

• The prior knowledge of oxidation numbers (ONs) for all elements of the system is not required; this fact is of capital importance when 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 (eq. 1).

where all 'fans' (K^* elements or cores) of the system are involved; $K^* = K$ for a non-redox system, $K^* < K$ for a redox system, where $K–K^*$ players are involved. When d_k are equal to the oxidation numbers (ONs) of elements in the corresponding 'fans' (k=1,…,K) of a non-redox system, then LC is transformed into identity, 0 = 0. For a redox system, LC assumes there simpler/simplest form, where only the species and components related to players are involved. The f_{12} is considered as the primary form of GEB, f_{12} = pr-GEB. The f_{12}, LC and any other combination $\sum_{k=3}^{K} a_k \cdot f_k - (f_{12} + a_0 \cdot f_0)$, where $a_k \in \mathbb{R}$, have full properties of GEB, although the simplest/shortest form of GEB, involving the smallest number of components, is more desirable.

• The criterion distinguishing between non-redox and redox systems is valid for redox systems of any degree of complexity. We can check it also on more complex redox systems, of any degree of complexity, where two or more electron-active elements as 'players' are involved. The relation (12) was also confirmed for electrolytic systems in binary and (generally) mixed-solvent A_s (s = 1, …, S) media [47], [48], [49], where mixed solvates

$$X_i^{z_i} \cdot n_{iA_1} \ldots n_{iA_s} \ldots n_{iA_S}$$

are assumed, and $n_{iAs} \geq 0$ is the mean number of A_s molecules attached to

$$\left[X_i^{z_i}\right]$$

• 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.

Final Comments

The GEB concept, discovered by Michałowski as the Approaches I (1992, [2], [3], [4]) and II (2005, [8]) to GEB, is perceived as the law of the matter conservation, as the general Law of Nature [27], as the hidden connection of physicochemical laws, and as a breakthrough in thermodynamic theory of electrolytic redox systems. The GATES/GEB formulated in 1992 is an example of an 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 of them were thoroughly criticized in our review papers [15], [16], [17], and elsewhere.

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 [50], [51], [52], here 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 understanding far better the physicochemical phenomena occurring in the system in question, and improving 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 ([26], pp. 361-363) 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 and non-aqueous media, with amphiprotic (co)solvents involved.

Notations and Acronyms:

D – titrand (solution titrated),

GATES – Generalized Approach to Electrolytic Systems,

GEB – Generalized Electron Balance,

ON – oxidation number,

T – titrant,

V – volume (mL) of T,

V_0 – volume (mL) of D.

Competing Interests

The authors have declared that no competing interests exist.

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