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Research Article

Oxidation Number, Oxidant and Reductant as Derivative Concepts Within GATES/GEB Formulation

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Abstract

Formulation of Generalized Electron Balance (GEB) according to Approach II to GEB, based on linear combination $f_{12} = 2 \cdot f(O) - f(H)$ of elemental balances: $f(H)$ for H and $f(O)$ for O, is illustrated on the titration of $NaBr + H_2SO_4$ (as titrand, D) with $Ce(SO_4)_2 + H_2SO_4$ solution (as titrant, T), according to GATES/GEB principles. Some fundamental advantages inherent in linear combination of f_{12} with other elemental/core balances are indicated. The prior information on oxidation numbers of all elements participating the redox system is not needed. The multipliers needed to obtain the simpler form of the balance resulting from the linear combination are equal to oxidation numbers of the elements participating the related system. This way, the f_{12} provides the criterion distinguishing between non-redox and redox systems. The f_{12} is linearly independent on other balances in a redox system, or linearly dependent in non-redox systems; the D and T are considered here as non-redox subsystems of the D+T redox system. All available physicochemical knowledge related to the D+T system can be involved in the iterative computer program used for calculation purposes.

Keywords

Redox titration; GATES/GEB; Linear combination; Oxidation number

Introduction

Redox systems are the most important/complex electrolytic systems. Redox reactions are usually coupled with acid-base, and – frequently – with complexation and/or precipitation reactions. There are redox systems with one (disproportionation, symproportionation), two or more electron-active elements. Moreover, a particular type (e.g. complexation) reaction may be exemplified by different representatives (here: ligands).

The commonly known viewpoint on titrations in electrolytic redox systems was introduced mainly in the 1960s in a series of papers by Bard and Simonsen [1], Bishop [2,3], followed by the articles of Goldman [4-10], and outlined later by Goldman [11]. The viewpoint (well-being) of those authors on their own achievements in this regard, expressed (among others) in the titles of their papers, was so amazingly contagious and convincing for the next generations of chemists, that it was replicated in numerous papers and handbooks issued later, e.g. [12-14], and in learning materials, available today in the Internet. Those elaborations/viewpoints, based on stoichiometric inferences, were totally criticized/disqualified in the review paper [15], and in [16-20].

The correct resolution of electrolytic redox systems, made according to the principles of Generalized Approach to Electrolytic Systems (GATES) [21], was presented in [15-46]. When referred to redox systems, GATES, involves the Generalized Electron Balance (GEB) in the software denoted as GATES/GEB.

Within the GATES formulation, the species in an electrolytic system are considered in their natural forms, particularly as hydrates $X_i^{z_i} \cdot n_{iW}$ in aqueous solutions [16] (p. 520), where z_i ($z_i = 0, \pm 1, \pm 2,...$) is the charge of $X_i^{z_i}$, expressed in terms of elementary charge unit $e = F/N_A$ (F – Faraday constant, N_A – Avogadro's constant); $n_i \equiv n_{iW} \equiv n_i H_2O$ (≥ 0) is the mean number of water (W = H_2O) 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 for elements or cores.

The terms: components and species are distinguished. 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 the static or dynamic D+T system, from titrand D and titrant T composed separately. The mono- or two-phase electrolytic 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), denoted briefly as $X_i^{z_i}$ (N_i, n_i); then we have: H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3),... .

The process considered is the titration, where V_0 mL of titrand D is titrated with V mL of titrant T; V is the volume of T added up to a defined point of the titration; the D and T are considered as subsystems of the D+T mixture thus formed. The volume of D+T at this point of the titration is V_0+V, if the assumption of additivity in volumes is admitted/tolerable. The N_i species $X_i^{z_i} \cdot n_i H_2O$ in the D+T mixture are denoted as $X_i^{z_i}$ (N_i, n_i), i=2,...,I, whose molar [mol/L] concentrations are denoted as $[X_i^{z_i}]$, and

$$\left(V_0 + V\right) \cdot \left[X_i^{z_i}\right] = 10^3 \cdot N_i / N_A \qquad (1)$$

Some species in a system may involve a core, i.e., a common group/cluster of elements with defined composition, structure and external charge, that is unchanged during a process realized in the system. For example, in $Ce(SO_4)_2$ (C) + H_2SO_4 (C_1) solution, applied as a titrant T in cerimetric [47] titrations we have, among others, the hydrated species of: HSO_4^{-1}, SO_4^{-2}, $CeSO_4^{+2}$, $Ce(SO_4)_2$ and $Ce(SO_4)_3^{-2}$, with SO_4^{-2} as the common core.

Balancing of electrolytic systems according to GATES/GEB principles

When balancing an electrolytic system, where K different elements/cores are involved, we apply the rules of:

(a) charge conservation, expressed by charge balance, f_0 = ChB, and

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(b) elements/cores conservation, termed as elemental/core balances, $f_k = f(Y_k)$,

where Y_k is an element or core of k-th kind (k=1,…,K); in particular, we have: $f_1 = f(H)$ for $Y_1 = H$, $f_2 = f(O)$ for $Y_2 = O$.

The numbers N_i of the species are interrelated in the charge balance, $f_0 = ChB$,

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

In fact, only charged species ($z_i \neq 0$) enter Equation 2. The N_i and N_{0j} are interrelated in elemental/core balances f_k, written as follows

$$f_k : \sum_{i=1}^{I} a_{ki} \cdot N_i - \sum_{j=1}^{J} d_{kj} \cdot N_{0j} = 0 \quad (k=1,…,K) \qquad (3)$$

In particular, we have:

$$a_{1i} = \alpha_{1i} + 2 \cdot n_i \qquad (4)$$

for H (k=1), where α_{1i} is the number of H-atoms involved in $X_i^{z_i}$, and

$$a_{2i} = \alpha_{2i} + n_i \qquad (5)$$

for O (k=2), where α_{2i} is the number of O-atoms involved in $X_i^{z_i}$. Then from Equations 4, 5 we get:

$$2 \cdot a_{2i} - a_{1i} = 2 \cdot \alpha_{2i} - \alpha_{1i} \qquad (6)$$

i.e., the numbers n_i of water molecules are cancelled, at any i-value. From Equations 3, 6 we have the balance

$$f_{12} = 2 \cdot f_2 - f_1 : \sum_{i=1}^{I} (2 \cdot \alpha_{2i} - \alpha_{1i}) \cdot N_i - \sum_{j=1}^{J} (2 \cdot d_{2j} - d_{1j}) \cdot N_{0j} = 0 \ (7)$$

where d_{1j} and d_{2j} are the numbers of atoms: H and O, resp. in one molecule of the j-th component Y_{0j}. For k=3,…,K, a_{ki} is a number of elements/cores of i-th kind in $X_i^{z_i}$, and d_{kj} (k=1,…,K) is a number of elements/cores of k-th kind in Y_{0j}. Linear combination of the balances: 2, 7 and 3 for k=3,…,κ, where κ ≤ K, with pre-assumed coefficients/multipliers m_k, gives

$$f_{12} + f_0 - \sum_{k=3}^{\kappa} m_k \cdot f_k = 0 \leftrightarrow -f_{12} + \sum_{k=3}^{\kappa} m_k \cdot f_k - f_0 = 0 \leftrightarrow (8)$$

$$(+1) \cdot f_1 + (-2) \cdot f_2 + \sum_{k=3}^{\kappa} m_k \cdot f_k - f_0 = 0 \leftrightarrow \qquad (9)$$

$$\left((+1) \cdot \alpha_{1i} + (-2) \cdot \alpha_{2i} + \sum_{k=3}^{\kappa} m_k \cdot a_{ki} - z_i \right) \cdot N_i = \sum \quad \left((+1) \cdot d_{1j} + (-2) \cdot d_{2j} - \sum_{k}^{\kappa} m_k \cdot d_{kj} \right) \cdot N_{0j} \ (10)$$

When the multipliers m_k are equal to the oxidation numbers of elements in the corresponding balances (3) for k=3,…, κ, we get the simpler(st) forms of the linear combinations, not involving the species composed only from electron-non-active elements. Note that $m_1 = +1$ and $m_2 = -2$ in Equation 10 are the oxidation numbers for H and O in components and the species of the system in question [47].
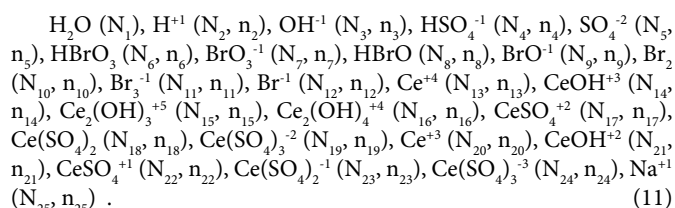
It is advisable to start formulation of the system from balances interrelating the numbers N_{0j} of particular components Y_j forming V_0 mL of titrand (D) and V mL of titrant (T) and the numbers N_i of particular species $X_i^{z_i} \cdot n_i H_2O$ formed in the D+T mixture, at a given point of the titration.

This article refers immediately to a dynamic redox system, considered in [48] according to the old viewpoint, commented above. The system will be formulated here according to GATES/GEB principles.

On cerimetric titration of bromide

Referring to the example raised in [48], we consider V_0 mL of titrand D composed of: NaBr (N_{01} molecules), H_2SO_4 (N_{02} molecules) and H_2O (N_{03} molecules), titrated with V mL of titrant T composed of Ce(SO$_4$)$_2$·4H$_2$O (N_{04} molecules), H_2SO_4 (N_{05} molecules) and H_2O

(N_{06} molecules). In $V_0 + V$ mL of the D+T mixture thus formed we have the species:

H_2O (N_1), H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3), HSO_4^{-1} (N_4, n_4), SO_4^{-2} (N_5, n_5), $HBrO_3$ (N_6, n_6), BrO_3^{-1} (N_7, n_7), $HBrO$ (N_8, n_8), BrO^{-1} (N_9, n_9), Br_2 (N_{10}, n_{10}), Br_3^{-1} (N_{11}, n_{11}), Br^{-1} (N_{12}, n_{12}), Ce^{+4} (N_{13}, n_{13}), $CeOH^{+3}$ (N_{14}, n_{14}), $Ce_2(OH)_3^{+5}$ (N_{15}, n_{15}), $Ce_2(OH)_4^{+4}$ (N_{16}, n_{16}), $CeSO_4^{+2}$ (N_{17}, n_{17}), $Ce(SO_4)_2$ (N_{18}, n_{18}), $Ce(SO_4)_3^{-2}$ (N_{19}, n_{19}), Ce^{+3} (N_{20}, n_{20}), $CeOH^{+2}$ (N_{21}, n_{21}), $CeSO_4^{+1}$ (N_{22}, n_{22}), $Ce(SO_4)_2^{-1}$ (N_{23}, n_{23}), $Ce(SO_4)_3^{-3}$ (N_{24}, n_{24}), Na^{+1} (N_{25}, n_{25}) .

$$(11)$$

Note, for example, that:

N_6 species of $HBrO_3 \cdot n_6 H_2O$, denoted for brevity as $HBrO_3$ (N_6, n_6), involve: $N_6(1+2n_6)$ atoms of H, $N_6(3+n_6)$ atoms of O, and N_6 atoms of Br;

N_{04} molecules of Ce(SO$_4$)$_2$·4H$_2$O involve: $8N_{04}$ atoms of H, $12N_{04}$ atoms of O and O, $2N_{04}$ atoms of S, and N_{04} atoms of Ce.

As we see, different species are considered in their natural form, i.e. as solvates, e.g. hydrates in aqueous media. These remarks can be extended also on binary- [34,49-51] and mixed-solvent media [29,52], where formation of the species $X_i^{z_i} \cdot n_{iA_1} \cdots n_{iA_S}$ ($n_{iA_S} \geq 0$) is admitted, assuming that at least one of the co-solvents A_s (s ∈ <1,S>) has amphiprotic properties.

Applying, for the convenience of notation, the common enumeration of the species as one presented in the set (11), we formulate the balances, separately for D, T, and D+T. We will check the properties of linear combinations of charge and elemental/core balances for each of these three solutions. Separate balancing of D and T aims to show/prove that D and T, when treated as separate solutions, are here non-redox systems.

A very useful/effective manner for checking/stating the linear dependence of the balances is the transformation of an appropriate system of equations to the identity, 0 = 0 [17,42]. To facilitate these operations, we apply the equivalent forms of the starting equations $f(Y_k) = 0$:

$$f_k = f(Y_k) : \varphi(Y_k) - b_k = 0 \Leftrightarrow \varphi(Y_k) = b_k \Leftrightarrow$$

$$-f_k(Y_k) : -\varphi(Y_k) = -b_k \Leftrightarrow b_k = \varphi(Y_k)$$

In this notation, $f(Y_k)$ will be essentially treated not as the algebraic expression on the left side of the equation $f(Y_k) = 0$, but as an equation that can be expressed in alternative forms presented above. The equations in the form $\varphi(Y_k) - b_k = 0$ are applied in the minimization function of the computer program (Appendix).

Balancing of D

The balances for elements/species in D (NaBr + H_2SO_4 + H_2O) and their linear combinations are as follows:

$$f_0 = ChB : N_2 - N_3 - N_4 - 2N_5 - N_{12} + N_{25} = 0$$

$$f_1 = f(H) : 2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5 n_5 + 2N_{12}n_{12} + 2N_{25}n_{25} = 2N_{02} + 2N_{03}$$

$$f_2 = f(O) : N_1 + N_2 n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_{12}n_{12} + N_{25}n_{25} = 4N_{02} + N_{03}$$

$$-f_3 = -f(Na) : N_{01} = N_{25}$$

$$-f_4 = -f(SO_4) = -f(S) : \quad N_{02} = N_4 + N_5$$

$f_5 = f(\text{Br}) : N_{12} = N_{01}$

$f_{12} = 2 \cdot f_2 - f_1 : -N_2 + N_3 + 7N_4 + 8N_5 = 6N_{02}$

$2 \cdot f_2 - f_1 + f_0 - f_3 : 6N_4 + 6N_5 = 6N_{02}$

$2 \cdot f_2 - f_1 + f_0 - f_3 - 6f_4 + f_5 : 0 = 0$

Balancing of T

The balances for elements/species in T ($Ce(SO_4)_2 \cdot 4H_2O + H_2SO_4 + H_2O$) and their linear combinations are as follows:

$f_0 = \text{ChB} : N_2 - N_3 - N_4 - 2N_5 + 4N_{13} + 3N_{14} + 5N_{15} + 4N_{16} + 2N_{17} - 2N_{19} = 0$

$f_1 = f(\text{H}) : 2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + 2N_{13}n_{13} + N_{14}(1+2n_{14}) + N_{15}(3+2n_{15}) + N_{16}(4+2n_{16}) + 2N_{17}n_{17} + 2N_{18}n_{18} + 2N_{19}n_{19} = 8N_{04} + 2N_{05} + 2N_{06}$

$f_2 = f(\text{O}) : N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_{13}n_{13} + N_{13}(1+n_{14}) + N_{15}(3+n_{15}) + N_{16}(4+n_{16}) + N_{17}(4+n_{17})$

$+ N_{18}(8+n_{18}) + N_{19}(12+n_{19}) = 12N_{04} + 4N_{05} + N_{06}$

$-f_4 = -f(SO_4) : 2N_{04} + N_{05} = N_4 + N_5 + N_{17} + 2N_{18} + 3N_{19}$

$-f_6 = -f(\text{Ce}) : N_{04} = N_{13} + N_{14} + 2N_{15} + 2N_{16} + N_{17} + N_{18} + N_{19}$

$f_{12} = 2 \cdot f_2 - f_1 : -N_2 + N_3 + 7N_4 + 8N_5 + N_{14} + 3N_{15} + 4N_{16} + 8N_{17} + 16N_{18} + 24N_{19} = 16N_{04} + 6N_{05}$

$2 \cdot f_2 - f_1 + f_0 : 6N_4 + 6N_5 + 4N_{13} + 4N_{14} + 8N_{15} + 8N_{16} + 10N_{17} + 16N_{18} + 22N_{19} = 16N_{04} + 6N_{05}$

$2 \cdot f_2 - f_1 + f_0 - 6f_4 : 4N_{13} + 4N_{14} + 8N_{15} + 8N_{16} + 4N_{17} + 4N_{18} + 4N_{19} = 4N_{04}$

$2 \cdot f_2 - f_1 + f_0 - 6f_4 - 4f_6 : 0 = 0$

Balancing of D+T

$f_0 = \text{ChB} : N_2 - N_3 - N_4 - 2N_5 - N_7 - N_9 - N_{11} - N_{12} + 4N_{13} + 3N_{14} + 5N_{15} + 4N_{16} + 2N_{17} - 2N_{19} + 3N_{20} + 2N_{21} + N_{22} - N_{23} - 3N_{24} + N_{25} = 0$ (12)

$f_1 = f(\text{H}) : 2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(1+2n_6) + 2N_7n_7 + N_8(1+2n_8) + 2N_9n_9 + 2N_{10}n_{10} + 2N_{11}n_{11} + 2N_{12}n_{12} + 2N_{13}n_{13} + N_{14}(1+2n_{14}) + N_{15}(3+2n_{15}) + N_{16}(4+2n_{16}) + 2N_{17}n_{17} + 2N_{18}n_{18} + 2N_{19}n_{19} + 2N_{20}n_{20} + N_{21}(1+2n_{21}) + 2N_{22}n_{22} + 2N_{23}n_{23} + 2N_{24}n_{24} + 2N_{25}n_{25} = 2N_{02} + 2N_{03} + 8N_{04} + 2N_{05} + 2N_{06}$

$f_2 = f(\text{O}) : N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(1+n_8) + N_9(1+n_9) + N_{10}n_{10} + N_{11}n_{11} + N_{12}n_{12} + N_{13}n_{13} + N_{14}(1+n_{14}) + N_{15}(3+n_{15}) + N_{16}(4+n_{16}) + N_{17}(4+n_{17}) + N_{18}(8+n_{18}) + N_{19}(12+n_{19}) + N_{20}n_{20} + N_{21}(1+n_{21}) + N_{22}(4+n_{22}) + N_{23}(8+n_{23}) + N_{24}(12+n_{24}) + N_{25}n_{25} = 4N_{02} + N_{03} + 12N_{04} + 4N_{05} + N_{06}$

$-f_3 = -f(\text{Na}) : N_{01} = N_{25}$ (13)

$-f_4 = -f(SO_4) : N_{02} + 2N_{04} + N_{05} = N_4 + N_5 + N_{17} + 2N_{18} + 3N_{19} + N_{22} + 2N_{23} + 3N_{24}$ (14)

$f_5 = f(\text{Br}) : N_6 + N_7 + N_8 + N_9 + 2N_{10} + 3N_{11} + N_{12} = N_{01}$ (15)

$f_6 = f(\text{Ce}) : N_{13} + N_{14} + 2N_{15} + 2N_{16} + N_{17} + N_{18} + N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} = N_{04}$ (16)

On this basis we formulate the linear combinations of the balances:

$f_{12} = 2 \cdot f_2 - f_1 : -N_2 + N_3 + 7N_4 + 8N_5 + 5N_6 + 6N_7 + N_8 + 2N_9 + $

$N_{14} + 3N_{15} + 4N_{16} + 8N_{17} + 16N_{18} + 24N_{19} + N_{21} + 8N_{22} + 16N_{23} + 24N_{24} = 6N_{02} + 16N_{04} + 6N_{05}$ (17)

$2 \cdot f_2 - f_1 + f_0 - f_3 - 6f_4 :$

$5(N_6 + N_7) + (N_8 + N_9) - N_{11} - N_{12} + 4(N_{13} + N_{14} + 2N_{15} + 2N_{16} + N_{17} + N_{18} + N_{19}) + 3(N_{20} + N_{21} + N_{22} + N_{23} + N_{24})$

$= 4N_{04} - N_{01}$ (18)

$(2 \cdot f_2 - f_1 + f_0 - f_3 - 6 \cdot f_4 + f_5 - 4 \cdot f_6)/2 :$

$3(N_6 + N_7) + N_8 + N_9 + N_{10} + N_{11} = (N_{20} + N_{21} + N_{22} + N_{23} + N_{24})/2$ (19)

Applying atomic numbers: $Z_{Br} = 35$ for Br, $Z_{Ce} = 58$ for Ce, we get

$Z_{Br} \cdot f_5 - Z_{Ce} \cdot f_6 - (2 \cdot f_2 - f_1 + f_0 - f_3 - 6f_4) :$

$(Z_{Br}-5)(N_6 + N_7) + (Z_{Br}-1)(N_8 + N_9) + 2Z_{Br}N_{10} + (3Z_{Br}+1)N_{11} + (Z_{Br}+1)N_{12} + (Z_{Ce}-4)(N_{13} + N_{14} + 2N_{15} + 2N_{16} + N_{17} + N_{18} + N_{19}) + (Z_{Ce}-3)(N_{20} + N_{21} + N_{22} + N_{23} + N_{24}) = (Z_{Br}+1)N_{01} + (Z_{Ce}-4)N_{04}$ (20)

Applying the relations: Equation 1 and: $C_0V_0 = 10^3 \cdot N_{01}/N_A$, $CV = 10^3 \cdot N_{04}/N_A$, $C_{01}V_0 = 10^3 \cdot N_{02}/N_A$, $C_1V = 10^3 \cdot N_{05}/N_A$, from the balances (12) – (20) we obtain the relations expressed in terms of molar [mol/L] concentrations:

$[H^{+1}] - [OH^{-1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] - [BrO_3^{-1}] - [BrO^{-1}] - [Br_3^{-1}] - [Br^{-1}] + 4[Ce^{+4}] + 3[CeOH^{+3}] + 5[Ce_2(OH)_3^{+5}] + 4[Ce_2(OH)_4^{+4}] + 2[CeSO_4^{+2}] - 2[Ce(SO_4)_3^{-2}] + 3[Ce^{+3}] + 2[CeOH^{+2}] + [CeSO_4^{+1}] - [Ce(SO_4)_2^{-1}] - 3[Ce(SO_4)_3^{-3}] + [Na^{+1}] = 0$ (12a)

$[Na^{+1}] = C_0V_0/(V_0+V)$ (13a)

$[HSO_4^{-1}] + [SO_4^{-2}] + [CeSO_4^{+2}] + 2[Ce(SO_4)_2] + 3[Ce(SO_4)_3^{-2}] + [CeSO_4^{+1}] + 2[Ce(SO_4)_2^{-1}] + 3[Ce(SO_4)_3^{-3}]$

$= (2CV + C_1V + C_{01}V_0)/(V_0+V)$ (14a)

$[HBrO_3] + [BrO_3^{-1}] + [HBrO] + [BrO^{-1}] + 2[Br_2] + 3[Br_3^{-1}] + [Br^{-1}] = C_0V_0/(V_0+V)$ (15a)

$[Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}] + [Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}] = CV/(V_0+V)$ (16a)

$-[H^{+1}] + [OH^{-1}] + 7[HSO_4^{-1}] + 8[SO_4^{-2}] + 5[HBrO_3] + 6[BrO_3^{-1}] + [HBrO] + 2[BrO^{-1}] + [CeOH^{+3}] + 3[Ce_2(OH)_3^{+5}] + 4[Ce_2(OH)_4^{+4}] + 8[CeSO_4^{+2}] + 16[Ce(SO_4)_2] + 24[Ce(SO_4)_3^{-2}] + [CeOH^{+2}] + 8[CeSO_4^{+1}] + 16[Ce(SO_4)_2^{-1}] + 24[Ce(SO_4)_3^{-3}] = (6C_{01}V_0 + 16CV + 6C_1V)/(V_0+V)$ (17a)

$5([HBrO_3] + [BrO_3^{-1}]) + [HBrO] + [BrO^{-1}] - [Br_3^{-1}] - [Br^{-1}] + 4([Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) + 3([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) = (4C_0V_0 - CV)/(V_0+V)$ (18a)

$3([HBrO_3] + [BrO_3^{-1}]) + [HBrO] + [BrO^{-1}] + [Br_2] + [Br_3^{-1}] - ([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}])/2 = 0$ (19a)

The N_{01} and N_{04} were not involved in Equation 19 and then C_0 and C are not involved in Equation 19a.

$(Z_{Br}-5)([HBrO_3] + [BrO_3^{-1}]) + (Z_{Br}-1)([HBrO] + [BrO^{-1}]) + 2Z_{Br}[Br_2] + (3Z_{Br}+1)[Br_3^{-1}] + (Z_{Br}+1)[Br^{-1}] + (Z_{Ce}-4)([Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) + (Z_{Ce}-3)([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}]) = (Z_{Br}+1)C_0V_0 + (Z_{Ce}-4)CV)/(V_0+V)$ (20a)

The distinguishing role of $f_{12} = 2 \cdot f(O) - f(H)$

For all redox systems, any linear combination of $f_{12} = 2 \cdot f(O) - f(H)$ with charge balance $f_0 = ChB$ and other elemental/core balances $f_k = f(Y_k)$ $(k=3,\ldots,K)$ related to a redox system of any degree of complexity does not give the identity, $0 = 0$ [17,41,45]. The f_{12} is linearly dependent on $f_0, f_3,\ldots, f_K$ when related to non-redox systems. In other words, the set of K independent balances $f_0, f_{12}, f_3,\ldots, f_K$ is applied for a redox system, or a set of K–1 balances $f_0, f_3,\ldots, f_K$ 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 [17,28,45] of any degree of complexity, also in mixed-solvent media [29,49,52].

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

All the inferences made within GATES/GEB are based on firmly established physical, physicochemical and algebraic foundations.

A choice of the independent equations and variables

Equations (17a), (18a), (19a) and (20a), are equivalent forms of the Generalized Electron Balance (GEB). This equivalence is perceived from the viewpoint of the linear combination of f_{12} with the balances related to the system in question. For calculations we take one of these equations. In the computer program in Appendix, the shortest balance expressed by Equation 19a, has been chosen.

The GEB (Equation 19a) completes the set of equations composed of charge balance (12a) and concentration balances for: Br (Equation 15a), Ce (Equation 16a), S (14a) – together 5 equations. The balance 13a, involving only one species, is not considered as equation, but as an equality [47], as a number that can be put, as such, into Equation 12a.

The set of independent variables is arranged in the (transposed) vector $\mathbf{x} = (E, pH, pSO4, pBr, pCe3)^T$, where E – potential [V], pH = $-\log[H^{+1}]$, pSO4 = $-\log[SO_4^{-2}]$, pBr = $-\log[Br^{-1}]$, pCe3 = $-\log[Ce^{+3}]$. informally, E is ascribed to GEB, pH to ChB, and pSO4, pBr, pCe3 to the related concentration balances.

The number of the (independent, 'homogeneous') variables equals to the number of equations, 5 = 5; this ensures a unique solution of the equations related to the system in question, at the preset C_0, C, C_{01}, C_1 and V_0 values, and the V-value at which the calculations are realized, at defined step of the calculation procedure offered e.g. by MATLAB [21], and realized according to the iterative computer program presented in Appendix.

On this basis, the functional dependencies: E = E(Φ), pH = pH(Φ) and speciation curves $\log\left[X_i^{z_i}\right] = \Psi_i(\Phi)$ can be presented graphically for different species $X_i^{z_i}$, where $\Phi = \dfrac{CV}{C_0 V_0}$ is the fraction titrated; it introduces a kind of normalization (independency on V_0 value) in graphical presentation of the titrimetric procedure, compare with the

related plots drawn for D+T system, where $FeSO_4 + H_2SO_4$ solution as D is titrated with $Ce(SO_4)_2 + H_2SO_4$ solution as T [25,30].

The Approach II to GEB *versus* the Approach I to GEB

GEB is perceived as a law of the matter conservation, as a relatively new Law of Nature [16,21,42]. From historical viewpoint, two equivalent approaches to GEB were applied. The Approach I to GEB is based on a "card game" principle, with electron-active elements as "players", electron-non-active elements as "fans", and electrons as "money". This analogy is broadly and suggestively depicted in [42] (pp. 41-43). The transmission of electrons occurs between different species formed by players, whereas such transmission does not occur between fans (the fans' accounts are intact). Another version of GEB is the Approach II, formulated on the basis of linear combination $f_{12} = 2 \cdot f(O) - f(H)$, presented above.

In the D+T redox system considered here, Br and Ce are two electron-active elements, brought to the system in the salts: NaBr and $Ce(SO_4)_2 \cdot 4H_2O$; the elements: H, O, Na and S are considered here as 'fans'. W=H_2O (owner of fans: H and O) is neither oxidized nor reduced in this system. N_{01} molecules of NaBr brings into the system $(Z_{Br}+1)N_{01}$ bromine electrons, whereas N_{04} molecules of $Ce(SO_4)_2 \cdot 4H_2O$ brings here $(Z_{Ce}-4)N_{04}$ cerium electrons. The common pool of electrons brought here equals $(Z_{Br}+1)N_{01} + (Z_{Ce}-4)N_{04}$. A part of these electrons form new bromine species and new cerium species. It is involved with transmission of electrons as "money" between Br and Ce as "players". W=H_2O accompanies formation of oxidized forms of Br, e.g. $Br^{-1} + 3H_2O - 6e^{-1} = HBrO_3 + 5H^{+1}$. In this reaction, O does not change its oxidation number, that is equal –2 both in H_2O and in BrO_3^{-1}. Likewise, H does not change its oxidation number; it is equal +1 in H_2O and in H^{+1}. So, on a particular stage of D+T formation, N_6 entities of $HBrO_3 \cdot n_6 H_2O$ as the species formed in this reaction contains $(Z_{Br} - 5)N_6$ bromine electrons, … , N_{24} entities of $Ce(SO_4)_3^{-3} \cdot n_{24} H_2O$ contains $(Z_{Ce} - 3)N_{24}$ cerium electrons (see the set (2) and Equations 15, 16). Applying the summation similar to that shown in [42] (p. 22), we obtain Equation 20, and then Equation 20a. Knowing that in a system of compatible equations [17], the equation obtained by any linear combination of a given equation with other equations are equivalent to one another; we can thus conclude that the Approach I to GEB is equivalent to the Approach II to GEB [42].

GEB, charge and concentration balances, together with the set of independent equilibrium constants, provide the numerical algorithm, implemented to software packages that support advanced programming, such as MATLAB computing environment. The calculation procedure enables the desired relationships to be plotted in 2D or 3D space [36].

In the version presented above, the GEB applies to systems where no radioactive transformations occur, and the composition of a matter reflects the natural isotopic composition of individual elements. The elements preservation principle is referred to stable elements. However, an extension of GATES on some systems where nuclear (α, β^-, β^+, or electron capture) transformations of radioactive elements occur is possible, assuming the known decay scheme of these elements [15].

Comments on the Oxidation Numbers

The remarks resulting from the calculations presented above for D and T as the non-redox subsystems (when considered separately)

of the redox D+T system (as the mixture of D and T), can be summarized as follows.

(1) Within $f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(O) - f(H)$ (Equation 11), all numbers involved with water (W=H$_2$O), i.e., N_1, N_{03}, N_{06} and all $n_i = n_w$ values were cancelled in D, T and D+T in aqueous media; This is an extremely advantageous situation, when perceived from the calculation viewpoint.

(2) The linear combinations: $2 \cdot f_2 - f_1 + f_0 - f_3 - 6f_4 + f_5$ for the titrand D and $2 \cdot f_2 - f_1 + f_0 - 6f_4 - 4f_6$ for the titrant T, after multiplying by –1, can be presented in equivalent forms:

$$2 \cdot f_2 - f_1 + f_0 - f_3 - 6 \cdot f_4 + f_5 = 0 \Leftrightarrow (+1) \cdot f(H) + (-2) \cdot f(O) + (+1) \cdot f(Na) + (+6) \cdot f(SO_4) + (-1) \cdot f(Br) - f_0 = 0 \quad (21)$$

$$2 \cdot f_2 - f_1 + f_0 - 6f_4 - 4f_6 = 0 \Leftrightarrow (+1) \cdot f(H) + (-2) \cdot f(O) + (+4) \cdot f(Ce) + (+6) \cdot f(SO_4) - f_0 = 0 \quad (22)$$

are transformed into identity, 0 = 0. The appropriately selected multipliers of the corresponding balances are equal to the oxidation numbers of the elements in the corresponding species included in these balances.

(3) The linear combination $2 \cdot f_2 - f_1 + f_0 - f_3 - 6f_4$, involving all electron-non-active elements of the system, can be presented in equivalent forms:

$$2 \cdot f_2 - f_1 + f_0 - f_3 - 6f_4 = 0 \Leftrightarrow (+1) \cdot f(H) + (-2) \cdot f(O) + (+1) \cdot f(Na) + (+6) \cdot f(SO_4) - f_0 = 0 \quad (23)$$

This combination (Equation 18a) involves all components and species formed by the electron-active elements of the system in question; it can be rewritten into the equivalent form

$$(+5) \cdot ([HBrO_3] + [BrO_3^{-1}]) + (+1) \cdot ([HBrO] + [BrO^{-1}]) + 3 \cdot (-1/3) \cdot [Br_3^{-1}] + (-1) \cdot [Br^{-1}] + (+4) \cdot ([Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) + (+3) \cdot ([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) = ((+4) \cdot CV + (-1) \cdot C_0V_0)/(V_0+V) \quad (18b)$$

In other words, all the species involved with 'fans' (H, O, Na and S) were cancelled within the linear combination (23). As we see, the multipliers for concentrations of the corresponding electron-active elements (Br, Ce) in the related components and species in Equation 18b are equal to oxidation numbers of these elements in the components and species. It is the exciting property from the viewpoint of the oxidation number which, after all, is seen in chemistry as the contractual concept [55-57]. It follows naturally from a proper linear combination of charge and elemental balances, which result from the basic principles of charge and elements preservation. The Approach II shows that GEB is based on a reliable law of the elements conservation, and – in this regard – it is equally robust as equations for charge and concentration balances.

On the step of formulation of the balances according to GATES/GEB principles, the term "oxidation number" is not ascribed to any element in a complex species present in the system considered according to Approach II to GEB; in this context, it is the redundant concept only. A known composition of all the species, expressed by their formula and external charge, provides information sufficient to formulate the related balances. These facts are of capital importance when redox equilibria are involved, e.g., with complex organic species [17]. Different species, also radicals and ion-radicals, can be included in these balances. None information about a structure of the species is needed.

The terms: oxidant and reductant are also redundant terms, not necessary (not applicable) as starting terms for further considerations on a redox system [15]. However, the oxidation degree can easily be calculated for simple compounds and species and then the Approach I to GEB is more applicable for this purpose, as a shorter (from the viewpoint of derivation only!) form of GEB. It is the case in the example of D+T system presented in this paper.

Final Comments

The Generalized Electron Balance (GEB) concept, obligatory for description of redox systems and formulated by Michałowski as the Approach I (1992) and the Approach II (2006) to GEB, is fully compatible with charge balance (ChB) and concentration balances, and complete set of relations for the corresponding equilibrium constants.

A keystone for the overall, thermodynamic knowledge on electrolytic systems is the linear combination $f_{12} = 2 \cdot f(O) - f(H)$ of elemental balances: $f(H)$ for H and $f(O)$ for O. The $2 \cdot f(O) - f(H)$ can be formulated both for non-redox and redox systems, in aqueous, non-aqueous and mixed-solvent systems, with amphiprotic (co)solvent(s) involved. The independent equation for $2 \cdot f(O) - f(H)$, considered as the *pr*imary form of GEB, *pr*-GEB = $2 \cdot f(O) - f(H)$, is the basis of GEB formulation according to Approach II to GEB. The $2 \cdot f(O) - f(H)$ is linearly independent on ChB and other balances, for elements/cores $f(Y_m) \neq$ H, O, in any redox system. For any non-redox system, $2 \cdot f(O) - f(H)$ is linearly dependent on those balances. Then the linear independency/dependency of $2 \cdot f(O) - f(H)$ on the other balances is the general criterion distinguishing between redox and non-redox systems.

This manner of GEB formulation needs none prior information on oxidation numbers for elements in components forming a (static or dynamic) system and in the species of the system thus formed. Within GATES/GEB, the roles of oxidants and reductants are not indicated *a priori* at the stage of formulation of the related balances in redox systems.

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