

Generalized Electron Balance for Dynamic Redox Systems in Mixed-Solvent Media

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Abstract

A complex example of electrolytic redox system involving 47 species, 3 electron-active elements and five (3 amphiprotic + 2 aprotic) co-solvents, is presented. Mixed solvates of the species thus formed are admitted in the system considered. It is proved that the Generalized Electron Balance (GEB) in its simplest form obtained according to the Approach II to GEB is identical with the one obtained for aqueous media and binary-solvent system, and is equivalent to the Approach I to GEB.

Keywords

Electrolytic Redox Systems, Generalized Electron Balance, Mixed-Solvent Media

1. Introduction

Motto: “Everything should be made as simple as possible, but not simpler” [1].

In the previous issues [2]-[8] and in earlier papers cited therein, the concept of Generalized Electron Balance (GEB), completing the set of compatible equations necessary for quantitative/mathematical solution of electrolytic redox systems, was introduced as two alternative options, named as Approach I and Approach II to GEB. In both Approaches it is assumed/admitted, that all the species $X_i^{z_i}$ exist in an electrolytic system in their natural form, *i.e.*, as solvates. In particular, there are hydrates $X_i^{z_i} \cdot n_{iW}$ in aqueous (W = H₂O) media, $X_i^{z_i} \cdot n_{iW}n_{iA}$, $X_i^{z_i} \cdot n_{iW}n_{iB}$ or $X_i^{z_i} \cdot n_{iA}n_{iB}$ in binary-solvent media (W, A), (W, B) or (A, B) [9]-[11], respectively. The values of n_{iW} , n_{iA} and n_{iB} , considered as mean numbers of W, A and B attached to $X_i^{z_i}$, are unknown, in principle, and vary with the co-solvent(s) composition, and solute(s) concentration.

In this paper, we refer also to more complex media with the mixture of co-solvents: W, A, B, E and F. We assume that the co-solvents are mutually miscible and at least one of the co-solvents has amphiprotic properties

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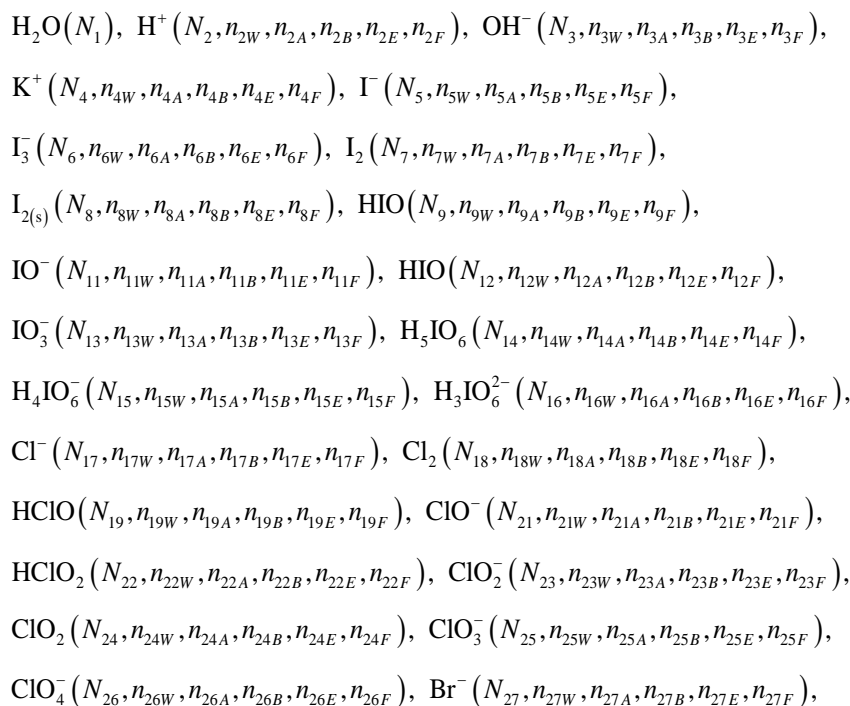
[5]. Each of the co-solvents has potential/real solvating properties, *i.e.*, $n_{iW}, n_{iA}, n_{iB}, n_{iE}, n_{iF} \geq 0$ in the solvated species $X_i^{z_i} \cdot n_{iW} n_{iA} n_{iB} n_{iE} n_{iF}$. Let $X_i^{z_i} (N_i, n_{iW}, n_{iA}, n_{iB}, n_{iE}, n_{iF})$ denotes N_i entities of these species in the related system. In further part of the paper, we assume $W = \text{H}_2\text{O}$, $A = \text{CH}_3\text{OH}$, $B = \text{C}_2\text{H}_5\text{OH}$, $E = (\text{CH}_3)_2\text{SO}$, $F = \text{CH}_3\text{CN}$; W , A , B have amphiprotic properties, and E , F —have not. In particular, N_{15} ions $\text{H}_4\text{IO}_6^- \cdot n_{15W} n_{15A} n_{15B} n_{15E} n_{15F}$ contain: $N_{15} (4 + 4n_{15A} + 6n_{15B} + 6n_{15E} + 3n_{15F})$ atoms of H , $N_{15} (6 + n_{15W} + n_{15A} + n_{15B} + n_{15E})$ atoms of O , N_{15} atoms of I , $N_{15} (n_{15A} + 2n_{15B} + 2n_{15E} + 2n_{15F})$ atoms of C , $N_{15} n_{15E}$ atoms of S , and $N_{15} n_{15F}$ atoms of N . It is assumed that the solvents do not form—with solvates—the species $X_i^{z_i}$ other than those formed in (known from) aqueous media. In other words, W , A , B , E , F enter (potentially) the solvating sphere of $X_i^{z_i}$. On this basis, the elemental balances $f(E(i))$ for particular elements $E(i)$ are formulated. For ordering purposes, we denote: $E(1) = \text{H}$, $E(2) = \text{O}$, $E(3) = \text{I}$, $E(4) = \text{C}$, $E(5) = \text{S}$, $E(6) = \text{N}$. We apply also the balances $f(C(Y))$ for the cores $C(Y)$, $Y = A, B, E, F$. The “core” is a cluster of elements of the same composition, structure and charge, that does not undergo a change in the system in question; e.g., CH_3OH , CH_3OH^+ and CH_3O^- contain the cluster CH_3O^- , considered as the core. We denote $C(A) = \text{CH}_3\text{O}^-$, $C(B) = \text{C}_2\text{H}_5\text{O}^-$, $C(E) = (\text{CH}_3)_2\text{SO} = \text{E}$, $C(F) = \text{CH}_5\text{CN} = \text{F}$. The species: H_2CO_3 , HCO_3^- and CO_3^{2-} have CO_3^{2-} as the common core. However, ClO_2^- (anion of HClO_2) and ClO_2 (chlorine dioxide) have different cores.

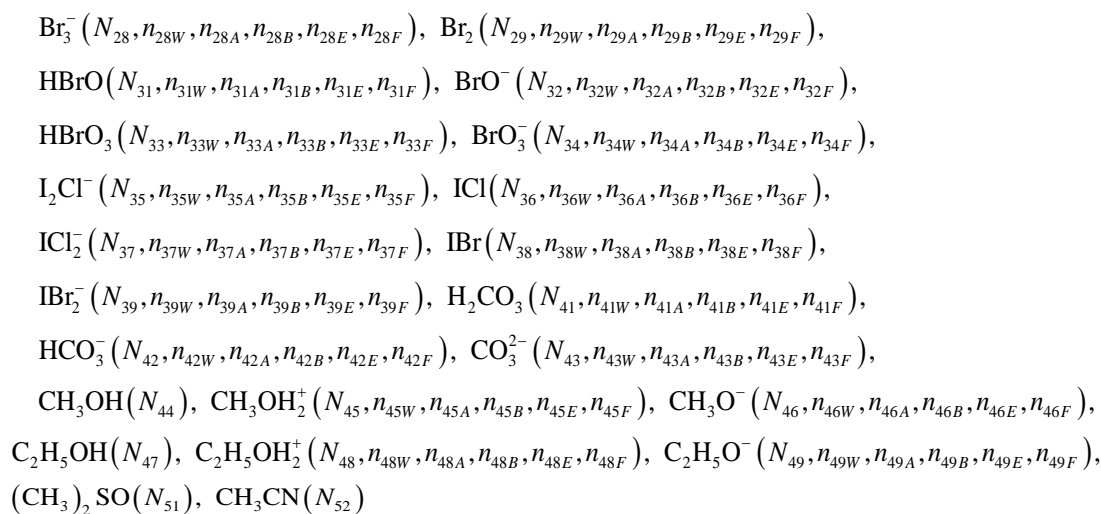
All the balances in this paper will be presented explicitly, to check the validity of the reasoning and accept it without reservations.

2. Formulation of Balances

Let us consider a system obtained after addition of V mL of titrant (T) containing I_2 (C) + KI (C_1) + CO_2 (C_2) in $A + B + E + F$ into V_0 mL of titrand (D) containing KBrO_3 (C_0) + HCl (C_{01}) + CO_2 (C_{02}) in $W + A + E$; all concentrations are expressed in mol/L. The volume V_0 mL of D is composed of N_{01} molecules of KBrO_3 , N_{02} molecules of HCl , N_{03} molecules of CO_2 , N_{04} molecules of W , N_{05} molecules of A , and N_{06} molecules of E ; V mL of T is composed of N_{07} molecules of I_2 , N_{08} molecules of KI , N_{09} molecules of CO_2 and N_{011} molecules of A , N_{012} molecules of B , N_{013} molecules of E , and N_{014} molecules of F .

We assume that the solutes composing D and T were introduced in single solvents or mixtures of solvents. In ca. $V_0 + V$ mL of a $D + T$ mixture thus obtained, we have the following species (all changes in oxidation degrees are admitted).





where $\text{I}_{2(s)}$ —solid iodine, I_2 —soluble iodine. In the above list of species, H_2O (N_1), CH_3OH (N_{44}), $\text{C}_2\text{H}_5\text{OH}$ (N_{47}), $(\text{CH}_3)_2\text{SO}$ (N_{51}) and CH_3CN (N_{52}) are free molecules of the corresponding solvents, *i.e.*, not involved in the solvates. We prove that the numbers: N_1 , N_{44} , N_{47} , N_{51} and N_{52} of the free molecules and the numbers: n_{iW} , n_{iA} , n_{iB} , n_{iE} , n_{iF} of these molecules in the solvates do not enter the simplest form of the resulting GEB.

The elemental balances: $f(\text{H})$ for H, and $f(\text{O})$ for O are as follows:

- $f(\text{H})$

$$\begin{aligned}
& 2N_1 + N_2 (1 + 2n_{2W} + 4n_{2A} + 6n_{2B} + 6n_{2E} + 3n_{2F}) + N_3 (1 + 2n_{3W} + 4n_{3A} + 6n_{3B} + 6n_{3E} + 3n_{3F}) \\
& + N_4 (2n_{4W} + 4n_{4A} + 6n_{4B} + 6n_{4E} + 3n_{4F}) + N_5 (2n_{5W} + 4n_{5A} + 6n_{5B} + 6n_{5E} + 3n_{5F}) \\
& + N_6 (2n_{6W} + 4n_{6A} + 6n_{6B} + 6n_{6E} + 3n_{6F}) + N_7 (2n_{7W} + 4n_{7A} + 6n_{7B} + 6n_{7E} + 3n_{7F}) \\
& + N_8 (2n_{8W} + 4n_{8A} + 6n_{8B} + 6n_{8E} + 3n_{8F}) + N_9 (1 + 2n_{9W} + 4n_{9A} + 6n_{9B} + 6n_{9E} + 3n_{9F}) \\
& + N_{11} (2n_{11W} + 4n_{11A} + 6n_{11B} + 6n_{11E} + 3n_{11F}) + N_{12} (1 + 2n_{12W} + 4n_{12A} + 6n_{12B} + 6n_{12E} + 3n_{12F}) \\
& + N_{13} (2n_{13W} + 4n_{13A} + 6n_{13B} + 6n_{13E} + 3n_{13F}) + N_{14} (5 + 2n_{14W} + 4n_{14A} + 6n_{14B} + 6n_{14E} + 3n_{14F}) \\
& + N_{15} (4 + 2n_{15W} + 4n_{15A} + 6n_{15B} + 6n_{15E} + 3n_{15F}) + N_{16} (3 + 2n_{16W} + 4n_{16A} + 6n_{16B} + 6n_{16E} + 3n_{16F}) \\
& + N_{17} (2n_{17W} + 4n_{17A} + 6n_{17B} + 6n_{17E} + 3n_{17F}) + N_{18} (2n_{18W} + 4n_{18A} + 6n_{18B} + 6n_{18E} + 3n_{18F}) \\
& + N_{19} (1 + 2n_{19W} + 4n_{19A} + 6n_{19B} + 6n_{19E} + 3n_{19F}) + N_{21} (2n_{21W} + 4n_{21A} + 6n_{21B} + 6n_{21E} + 3n_{21F}) \\
& + N_{22} (1 + 2n_{22W} + 4n_{22A} + 6n_{22B} + 6n_{22E} + 3n_{22F}) + N_{23} (2n_{23W} + 4n_{23A} + 6n_{23B} + 6n_{23E} + 3n_{23F}) \\
& + N_{24} (2n_{24W} + 4n_{24A} + 6n_{24B} + 6n_{24E} + 3n_{24F}) + N_{25} (2n_{25W} + 4n_{25A} + 6n_{25B} + 6n_{25E} + 3n_{25F}) \\
& + N_{26} (2n_{26W} + 4n_{26A} + 6n_{26B} + 6n_{26E} + 3n_{26F}) + N_{27} (2n_{27W} + 4n_{27A} + 6n_{27B} + 6n_{27E} + 3n_{27F}) \\
& + N_{28} (2n_{28W} + 4n_{28A} + 6n_{28B} + 6n_{28E} + 3n_{28F}) + N_{29} (2n_{29W} + 4n_{29A} + 6n_{29B} + 6n_{29E} + 3n_{29F}) \\
& + N_{31} (1 + 2n_{31W} + 4n_{31A} + 6n_{31B} + 6n_{31E} + 3n_{31F}) + N_{32} (2n_{32W} + 4n_{32A} + 6n_{32B} + 6n_{32E} + 3n_{32F}) \\
& + N_{33} (1 + 2n_{33W} + 4n_{33A} + 6n_{33B} + 6n_{33E} + 3n_{33F}) + N_{34} (2n_{34W} + 4n_{34A} + 6n_{34B} + 6n_{34E} + 3n_{34F}) \\
& + N_{35} (2n_{35W} + 4n_{35A} + 6n_{35B} + 6n_{35E} + 3n_{35F}) + N_{36} (2n_{36W} + 4n_{36A} + 6n_{36B} + 6n_{36E} + 3n_{36F}) \\
& + N_{37} (2n_{37W} + 4n_{37A} + 6n_{37B} + 6n_{37E} + 3n_{37F}) + N_{38} (2n_{38W} + 4n_{38A} + 6n_{38B} + 6n_{38E} + 3n_{38F}) \\
& + N_{39} (2n_{39W} + 4n_{39A} + 6n_{39B} + 6n_{39E} + 3n_{39F}) + N_{41} (2 + 2n_{41W} + 4n_{41A} + 6n_{41B} + 6n_{41E} + 3n_{41F}) \\
& + N_{42} (1 + 2n_{42W} + 4n_{42A} + 6n_{42B} + 6n_{42E} + 3n_{42F}) + N_{43} (2n_{43W} + 4n_{43A} + 6n_{43B} + 6n_{43E} + 3n_{43F}) + 4N_{44} \quad (1) \\
& + N_{45} (5 + 2n_{45W} + 4n_{45A} + 6n_{45B} + 6n_{45E} + 3n_{45F}) + N_{46} (3 + 2n_{46W} + 4n_{46A} + 6n_{46B} + 6n_{46E} + 3n_{46F}) + 6N_{47} \\
& + N_{48} (7 + 2n_{48W} + 4n_{48A} + 6n_{48B} + 6n_{48E} + 3n_{48F}) + N_{49} (5 + 2n_{49W} + 4n_{49A} + 6n_{49B} + 6n_{49E} + 3n_{49F}) \\
& + 6N_{51} + 3N_{52} = N_{02} + 2N_{04} + 4N_{05} + 6N_{06} + 4N_{011} + 6N_{012} + 6N_{013} + 3N_{014}
\end{aligned}$$

• $f(O)$

$$\begin{aligned}
 & N_1 + N_2 (n_{2W} + n_{2A} + n_{2B} + n_{2E}) + N_3 (1 + n_{3W} + n_{3A} + n_{3B} + n_{3E}) + N_4 (n_{4W} + n_{4A} + n_{4B} + n_{4E}) \\
 & + N_5 (n_{5W} + n_{5A} + n_{5B} + n_{5E}) + N_6 (n_{6W} + n_{6A} + n_{6B} + n_{6E}) + N_7 (n_{7W} + n_{7A} + n_{7B} + n_{7E}) \\
 & + N_8 (n_{8W} + n_{8A} + n_{8B} + n_{8E}) + N_9 (1 + n_{9W} + n_{9A} + n_{9B} + n_{9E}) + N_{11} (1 + n_{11W} + n_{11A} + n_{11B} + n_{11E}) \\
 & + N_{12} (3 + n_{12W} + n_{12A} + n_{12B} + n_{12E}) + N_{13} (3 + n_{13W} + n_{13A} + n_{13B} + n_{13E}) + N_{14} (6 + n_{14W} + n_{14A} + n_{14B} + n_{14E}) \\
 & + N_{15} (6 + n_{15W} + n_{15A} + n_{15B} + n_{15E}) + N_{16} (6 + n_{16W} + n_{16A} + n_{16B} + n_{16E}) + N_{17} (n_{17W} + n_{17A} + n_{17B} + n_{17E}) \\
 & + N_{18} (n_{18W} + n_{18A} + n_{18B} + n_{18E}) + N_{19} (1 + n_{19W} + n_{19A} + n_{19B} + n_{19E}) + N_{21} (1 + n_{21W} + n_{21A} + n_{21B} + n_{21E}) \\
 & + N_{22} (2 + n_{22W} + n_{22A} + n_{22B} + n_{22E}) + N_{23} (2 + n_{23W} + n_{23A} + n_{23B} + n_{23E}) + N_{24} (2 + n_{24W} + n_{24A} + n_{24B} + n_{24E}) \\
 & + N_{25} (3 + n_{25W} + n_{25A} + n_{25B} + n_{25E}) + N_{26} (4 + n_{26W} + n_{26A} + n_{26B} + n_{26E}) + N_{27} (n_{27W} + n_{27A} + n_{27B} + n_{27E}) \\
 & + N_{28} (n_{28W} + n_{28A} + n_{28B} + n_{28E}) + N_{29} (n_{29W} + n_{29A} + n_{29B} + n_{29E}) + N_{31} (1 + n_{31W} + n_{31A} + n_{31B} + n_{31E}) \\
 & + N_{32} (1 + n_{32W} + n_{32A} + n_{32B} + n_{32E}) + N_{33} (3 + n_{33W} + n_{33A} + n_{33B} + n_{33E}) + N_{34} (3 + n_{34W} + n_{34A} + n_{34B} + n_{34E}) \\
 & + N_{35} (n_{35W} + n_{35A} + n_{35B} + n_{35E}) + N_{36} (n_{36W} + n_{36A} + n_{36B} + n_{36E}) + N_{37} (n_{37W} + n_{37A} + n_{37B} + n_{37E}) \\
 & + N_{38} (n_{38W} + n_{38A} + n_{38B} + n_{38E}) + N_{39} (n_{39W} + n_{39A} + n_{39B} + n_{39E}) + N_{41} (3 + n_{41W} + n_{41A} + n_{41B} + n_{41E}) \\
 & + N_{42} (3 + n_{42W} + n_{42A} + n_{42B} + n_{42E}) + N_{43} (3 + n_{43W} + n_{43A} + n_{43B} + n_{43E}) \\
 & + N_{44} + N_{45} (1 + n_{45W} + n_{45A} + n_{45B} + n_{45E}) + N_{46} (1 + n_{46W} + n_{46A} + n_{46B} + n_{46E}) \\
 & + N_{47} + N_{48} (1 + n_{48W} + n_{48A} + n_{48B} + n_{48E}) + N_{49} (1 + n_{49W} + n_{49A} + n_{49B} + n_{49E}) + N_{51} \\
 & = 3N_{01} + 2N_{03} + N_{04} + N_{05} + N_{06} + 2N_{09} + N_{011} + N_{012} + N_{013}
 \end{aligned} \tag{2}$$

From (1) and (2) we obtain

• $2 \cdot f(O) - f(H)$

$$\begin{aligned}
 & N_2 (-1 - 2n_{2A} - 4n_{2B} - 4n_{2E} - 3n_{2F}) + N_3 (1 - 2n_{3A} - 4n_{3B} - 4n_{3E} - 3n_{3F}) + N_4 (-2n_{4A} - 4n_{4B} - 4n_{4E} - 3n_{4F}) \\
 & + N_5 (-2n_{5A} - 4n_{5B} - 4n_{5E} - 3n_{5F}) + N_6 (-2n_{6A} - 4n_{6B} - 4n_{6E} - 3n_{6F}) + N_7 (-2n_{7A} - 4n_{7B} - 4n_{7E} - 3n_{7F}) \\
 & + N_8 (-2n_{8A} - 4n_{8B} - 4n_{8E} - 3n_{8F}) + N_9 (1 - 2n_{9A} - 4n_{9B} - 4n_{9E} - 3n_{9F}) + N_{11} (2 - 2n_{11A} - 4n_{11B} - 4n_{11E} - 3n_{11F}) \\
 & + N_{12} (5 - 2n_{12A} - 4n_{12B} - 4n_{12E} - 3n_{12F}) + N_{13} (6 - 2n_{13A} - 4n_{13B} - 4n_{13E} - 3n_{13F}) \\
 & + N_{14} (7 - 2n_{14A} - 4n_{14B} - 4n_{14E} - 3n_{14F}) + N_{15} (8 - 2n_{15A} - 4n_{15B} - 4n_{15E} - 3n_{15F}) \\
 & + N_{16} (9 - 2n_{16A} - 4n_{16B} - 4n_{16E} - 3n_{16F}) + N_{17} (-2n_{17A} - 4n_{17B} - 4n_{17E} - 3n_{17F}) \\
 & + N_{18} (-2n_{18A} - 4n_{18B} - 4n_{18E} - 3n_{18F}) + N_{19} (1 - 2n_{19A} - 4n_{19B} - 4n_{19E} - 3n_{19F}) \\
 & + N_{21} (2 - 2n_{21A} - 4n_{21B} - 4n_{21E} - 3n_{21F}) + N_{22} (3 - 2n_{22A} - 4n_{22B} - 4n_{22E} - 3n_{22F}) \\
 & + N_{23} (4 - 2n_{23A} - 4n_{23B} - 4n_{23E} - 3n_{23F}) + N_{24} (4 - 2n_{24A} - 4n_{24B} - 4n_{24E} - 3n_{24F}) \\
 & + N_{25} (6 - 2n_{25A} - 4n_{25B} - 4n_{25E} - 3n_{25F}) + N_{26} (8 - 2n_{26A} - 4n_{26B} - 4n_{26E} - 3n_{26F}) \\
 & + N_{27} (-2n_{27A} - 4n_{27B} - 4n_{27E} - 3n_{27F}) + N_{28} (-2n_{28A} - 4n_{28B} - 4n_{28E} - 3n_{28F}) \\
 & + N_{29} (-2n_{29A} - 4n_{29B} - 4n_{29E} - 3n_{29F}) + N_{31} (1 - 2n_{31A} - 4n_{31B} - 4n_{31E} - 3n_{31F}) \\
 & + N_{32} (2 - 2n_{32A} - 4n_{32B} - 4n_{32E} - 3n_{32F}) + N_{33} (5 - 2n_{33A} - 4n_{33B} - 4n_{33E} - 3n_{33F}) \\
 & + N_{34} (6 - 2n_{34A} - 4n_{34B} - 4n_{34E} - 3n_{34F}) + N_{35} (-2n_{35A} - 4n_{35B} - 4n_{35E} - 3n_{35F}) \\
 & + N_{36} (-2n_{36A} - 4n_{36B} - 4n_{36E} - 3n_{36F}) + N_{37} (-2n_{37A} - 4n_{37B} - 4n_{37E} - 3n_{37F}) \\
 & + N_{38} (-2n_{38A} - 4n_{38B} - 4n_{38E} - 3n_{38F}) + N_{39} (-2n_{39A} - 4n_{39B} - 4n_{39E} - 3n_{39F}) \\
 & + N_{41} (4 - 2n_{41A} - 4n_{41B} - 4n_{41E} - 3n_{41F}) + N_{42} (5 - 2n_{42A} - 4n_{42B} - 4n_{42E} - 3n_{42F}) \\
 & + N_{43} (6 - 2n_{43A} - 4n_{43B} - 4n_{43E} - 3n_{43F}) - 2N_{44} + N_{45} (-3 - 2n_{45A} - 4n_{45B} - 4n_{45E} - 3n_{45F}) \\
 & + N_{46} (-1 - 2n_{46A} - 4n_{46B} - 4n_{46E} - 3n_{46F}) - 2N_{47} \\
 & + N_{48} (-5 - 2n_{48A} - 4n_{48B} - 4n_{48E} - 3n_{48F}) + N_{49} (-3 - 2n_{49A} - 4n_{49B} - 4n_{49E} - 3n_{49F}) - 4N_{51} - 3N_{52} \\
 & = 6N_{01} - N_{02} + 4N_{03} - 2N_{05} - 4N_{06} + 4N_{09} - 2N_{011} - 4N_{012} - 4N_{013} - 3N_{014}
 \end{aligned} \tag{3}$$

As we see, Equation (3) does not involve the terms N_1 , N_{04} , and $\{n_{iW}\}$ related to water. To cancel the terms

involved with A, B, E and F, we add Equation (3) to the core balances (4) - (7): $2 \cdot f(\text{CH}_3\text{O})$ (4), $4 \cdot f(\text{C}_2\text{H}_5\text{O})$ (5), $4 \cdot f((\text{CH}_3)_2\text{SO})$ (6), $3 \cdot f(\text{CH}_3\text{CN})$ (7) and charge balance (8). Further simplification gives addition of the balance for K (9), and of the core balance $4 \cdot f(\text{CO}_3)$ (10):

- $2 \cdot f(\text{CH}_3\text{O})$

$$\begin{aligned} & 2N_2n_{2A} + 2N_3n_{3A} + 2N_4n_{4A} + 2N_5n_{5A} + 2N_6n_{6A} + 2N_7n_{7A} + 2N_8n_{8A} + 2N_9n_{9A} + 2N_{11}n_{11A} + 2N_{12}n_{12A} \\ & + 2N_{13}n_{13A} + 2N_{14}n_{14A} + 2N_{15}n_{15A} + 2N_{16}n_{16A} + 2N_{17}n_{17A} + 2N_{18}n_{18A} + 2N_{19}n_{19A} + 2N_{21}n_{21A} + 2N_{22}n_{22A} \\ & + 2N_{23}n_{23A} + 2N_{24}n_{24A} + 2N_{25}n_{25A} + 2N_{26}n_{26A} + 2N_{27}n_{27A} + 2N_{28}n_{28A} + 2N_{29}n_{29A} + 2N_{31}n_{31A} + 2N_{32}n_{32A} \\ & + 2N_{33}n_{33A} + 2N_{34}n_{34A} + 2N_{35}n_{35A} + 2N_{36}n_{36A} + 2N_{37}n_{37A} + 2N_{38}n_{38A} + 2N_{39}n_{39A} + 2N_{41}n_{41A} + 2N_{42}n_{42A} \\ & + 2N_{43}n_{43A} + 2N_{44} + N_{45}(2 + 2n_{45A}) + N_{46}(2 + 2n_{46A}) + 2N_{48}n_{48A} + 2N_{49}n_{49A} = 2N_{05} + 2N_{011} \end{aligned} \quad (4)$$

- $4 \cdot f(\text{C}_2\text{H}_5\text{O})$

$$\begin{aligned} & 4N_2n_{2B} + 4N_3n_{3B} + 4N_4n_{4B} + 4N_5n_{5B} + 4N_6n_{6B} + 4N_7n_{7B} + 4N_8n_{8B} + 4N_9n_{9B} + 4N_{11}n_{11B} + 4N_{12}n_{12B} \\ & + 4N_{13}n_{13B} + 4N_{14}n_{14B} + 4N_{15}n_{15B} + 4N_{16}n_{16B} + 4N_{17}n_{17B} + 4N_{18}n_{18B} + 4N_{19}n_{19B} + 4N_{21}n_{21B} + 4N_{22}n_{22B} \\ & + 4N_{23}n_{23B} + 4N_{24}n_{24B} + 4N_{25}n_{25B} + 4N_{26}n_{26B} + 4N_{27}n_{27B} + 4N_{28}n_{28B} + 4N_{29}n_{29B} + 4N_{31}n_{31B} + 4N_{32}n_{32B} \\ & + 4N_{33}n_{33B} + 4N_{34}n_{34B} + 4N_{35}n_{35B} + 4N_{36}n_{36B} + 4N_{37}n_{37B} + 4N_{38}n_{38B} + 4N_{39}n_{39B} + 4N_{41}n_{41B} + 4N_{42}n_{42B} \\ & + 4N_{43}n_{43B} + 4N_{45}n_{45B} + 4N_{46}n_{46B} + 4N_{47} + N_{48}(4 + 4n_{48B}) + N_{49}(4 + 4n_{49B}) = 4N_{012} \end{aligned} \quad (5)$$

- $4 \cdot f((\text{CH}_3)_2\text{SO})$

$$\begin{aligned} & 4N_2n_{2E} + 4N_3n_{3E} + 4N_4n_{4E} + 4N_5n_{5E} + 4N_6n_{6E} + 4N_7n_{7E} + 4N_8n_{8E} + 4N_9n_{9E} + 4N_{11}n_{11E} + 4N_{12}n_{12E} \\ & + 4N_{13}n_{13E} + 4N_{14}n_{14E} + 4N_{15}n_{15E} + 4N_{16}n_{16E} + 4N_{17}n_{17E} + 4N_{18}n_{18E} + 4N_{19}n_{19E} + 4N_{21}n_{21E} + 4N_{22}n_{22E} \\ & + 4N_{23}n_{23E} + 4N_{24}n_{24E} + 4N_{25}n_{25E} + 4N_{26}n_{26E} + 4N_{27}n_{27E} + 4N_{28}n_{28E} + 4N_{29}n_{29E} + 4N_{31}n_{31E} + 4N_{32}n_{32E} \\ & + 4N_{33}n_{33E} + 4N_{34}n_{34E} + 4N_{35}n_{35E} + 4N_{36}n_{36E} + 4N_{37}n_{37E} + 4N_{38}n_{38E} + 4N_{39}n_{39E} + 4N_{41}n_{41E} + 4N_{42}n_{42E} \\ & + 4N_{43}n_{43E} + 4N_{45}n_{45E} + 4N_{46}n_{46E} + 4N_{48}n_{48E} + 4N_{49}n_{49E} + 4N_{51} = 4N_{06} + 4N_{013} \end{aligned} \quad (6)$$

- $3 \cdot f(\text{CH}_3\text{CN})$

$$\begin{aligned} & 3N_2n_{2F} + 3N_3n_{3F} + 3N_4n_{4F} + 3N_5n_{5F} + 3N_6n_{6F} + 3N_7n_{7F} + 3N_8n_{8F} + 3N_9n_{9F} + 3N_{11}n_{11F} + 3N_{12}n_{12F} \\ & + 3N_{13}n_{13F} + 3N_{14}n_{14F} + 3N_{15}n_{15F} + 3N_{16}n_{16F} + 3N_{17}n_{17F} + 3N_{18}n_{18F} + 3N_{19}n_{19F} + 3N_{21}n_{21F} + 3N_{22}n_{22F} \\ & + 3N_{23}n_{23F} + 3N_{24}n_{24F} + 3N_{25}n_{25F} + 3N_{26}n_{26F} + 3N_{27}n_{27F} + 3N_{28}n_{28F} + 3N_{29}n_{29F} + 3N_{31}n_{31F} + 3N_{32}n_{32F} \\ & + 3N_{33}n_{33F} + 3N_{34}n_{34F} + 3N_{35}n_{35F} + 3N_{36}n_{36F} + 3N_{37}n_{37F} + 3N_{38}n_{38F} + 3N_{39}n_{39F} + 3N_{41}n_{41F} + 3N_{42}n_{42F} \\ & + 3N_{43}n_{43F} + 3N_{45}n_{45F} + 3N_{46}n_{46F} + 3N_{48}n_{48F} + 3N_{49}n_{49F} + 3N_{52} = 3N_{014} \end{aligned} \quad (7)$$

- Charge balance

$$\begin{aligned} & N_2 - N_3 + N_4 - N_5 - N_6 - N_{11} - N_{13} - N_{15} - 2N_{16} - N_{17} - N_{21} - N_{23} - N_{25} - N_{26} - N_{27} \\ & - N_{28} - N_{32} - N_{34} - N_{35} - N_{37} - N_{39} - N_{42} - 2N_{43} + N_{45} - N_{46} + N_{48} - N_{49} = 0 \end{aligned} \quad (8)$$

- $f(\text{K})$

$$N_{01} + N_{08} = N_4 \quad (9)$$

- $4 \cdot f(\text{CO}_3)$

$$4N_{03} + 4N_{09} = 4N_{41} + 4N_{42} + 4N_{43} \quad (10)$$

As the result of this addition, considered as a kind of linear combination [4], we obtain the simplest form of GEB, expressed in terms of numbers of entities:

$$\begin{aligned} & -N_5 - N_6 + N_9 + N_{11} + 5N_{12} + 5N_{13} + 7N_{14} + 7N_{15} + 7N_{16} - N_{17} + N_{19} + N_{21} + 3N_{22} + 3N_{23} + 4N_{24} \\ & + N_{25} + 7N_{26} - N_{27} - N_{28} + N_{31} + N_{32} + 5N_{33} + 5N_{34} - N_{35} - N_{37} - N_{39} = 5N_{01} - N_{02} - N_{08} \end{aligned} \quad (11)$$

Applying the relations:

$$\begin{aligned} [X_i^{z_i}](V_0 + V) &= 10^3 \cdot N_i / N_A, \quad C_0 V_0 = 10^3 \cdot N_{01} / N_A, \quad C_{01} V_0 = 10^3 \cdot N_{02} / N_A, \\ CV &= 10^3 \cdot N_{07} / N_A, \quad C_1 V = 10^3 \cdot N_{08} / N_A \end{aligned} \quad (12)$$

(where N_A —Avogadro's constant), from Equations (11), (12) we have

$$\begin{aligned} & -[I^-] - [I_3^-] + [HIO] + [IO^-] + 5[HIO_3] + 5[IO_3^-] + 7[H_5IO_6] + 7[H_4IO_6^-] + 7[H_3IO_6^{2-}] \\ & -[Cl^-] + [HClO] + [ClO^-] + 3[HClO_2] + 3[ClO_2^-] + 4[ClO_2] + 5[ClO_3^-] + 7[ClO_4^-] \\ & -[Br^-] - [Br_3^-] + [HBrO] + [BrO^-] + 5[HBrO_3] + 5[BrO_3^-] - [I_2Cl^-] - [ICl_2^-] - [IBr_2^-] \\ & = (5C_0V_0 - C_{01}V_0 - C_1V) / (V_0 + V) \end{aligned} \quad (13)$$

Elemental balances for electro-active elements ("players") are as follows:

$f(\text{Br})$

$$N_{27} + 3N_{28} + 2N_{29} + N_{31} + N_{32} + N_{33} + N_{34} + N_{38} + 2N_{39} = N_{01} \quad (14)$$

$f(\text{Cl})$

$$N_{17} + 2N_{18} + N_{19} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + N_{26} + N_{35} + N_{36} + 2N_{37} = N_{02} \quad (15)$$

$f(\text{I})$

$$\begin{aligned} & N_5 + 3N_6 + 2N_7 + 2N_8 + N_9 + N_{11} + N_{12} + N_{13} + N_{14} + N_{15} \\ & + N_{16} + 2N_{35} + N_{36} + N_{37} + N_{38} + N_{39} = 2N_{07} + N_{08} \end{aligned} \quad (16)$$

Multiplying (14) - (16) by atomic numbers: $Z_{\text{Br}} = 35$, $Z_{\text{Cl}} = 17$, $Z_{\text{I}} = 53$, for Br, Cl and I, respectively, adding them and applying Equation (12), we have:

$$\begin{aligned} & Z_{\text{I}}[I^-] + 3Z_{\text{I}}[I_3^-] + 2Z_{\text{I}}([I_2] + [I_{2(s)}]) + Z_{\text{I}}([HIO] + [IO^-]) + Z_{\text{I}}([HIO_3] + [IO_3^-]) \\ & + Z_{\text{I}}([H_5IO_6] + [H_4IO_6^-] + [H_3IO_6^{2-}]) + Z_{\text{Cl}}[Cl^-] + 2Z_{\text{Cl}}[Cl_2] + Z_{\text{Cl}}([HClO] + [ClO^-]) \\ & + Z_{\text{Cl}}([HClO_2] + [ClO_2^-]) + Z_{\text{Cl}}[ClO_2] + Z_{\text{Cl}}[ClO_3^-] + Z_{\text{Cl}}[ClO_4^-] \\ & + Z_{\text{Br}}[Br^-] + 3Z_{\text{Br}}[Br_3^-] + 2Z_{\text{Br}}[Br_2] + Z_{\text{Br}}([HBrO] + [BrO^-]) + Z_{\text{Br}}([HBrO_3] + [BrO_3^-]) \\ & + (2Z_{\text{I}} + Z_{\text{Cl}})[I_2Cl^-] + (Z_{\text{I}} + Z_{\text{Cl}})[ICl] + (Z_{\text{I}} + 2Z_{\text{Cl}})[ICl_2^-] + (Z_{\text{I}} + Z_{\text{Br}})[IBr] + (Z_{\text{I}} + 2Z_{\text{Br}})[IBr_2^-] \\ & = (Z_{\text{Br}}C_0V_0 + Z_{\text{Cl}}C_{01}V_0 + 2Z_{\text{I}}CV + Z_{\text{I}}C_1V) / (V_0 + V) \end{aligned} \quad (17)$$

After subtracting (13) from (17), we get the equation for GEB, identical with one obtained according to Approach I to GEB

$$\begin{aligned} & (Z_{\text{I}} + 1)[I^-] + (3Z_{\text{I}} + 1)[I_3^-] + 2Z_{\text{I}}([I_2] + [I_{2(s)}]) + (Z_{\text{I}} - 1)([HIO] + [IO^-]) + (Z_{\text{I}} - 5)([HIO_3] + [IO_3^-]) \\ & + (Z_{\text{I}} - 7)([H_5IO_6] + [H_4IO_6^-] + [H_3IO_6^{2-}]) + (Z_{\text{Cl}} + 1)[Cl^-] + 2Z_{\text{Cl}}[Cl_2] + (Z_{\text{Cl}} - 1)([HClO] + [ClO^-]) \\ & + (Z_{\text{Cl}} - 3)([HClO_2] + [ClO_2^-]) + (Z_{\text{Cl}} - 4)[ClO_2] + (Z_{\text{Cl}} - 5)[ClO_3^-] + (Z_{\text{Cl}} - 7)[ClO_4^-] \\ & + (Z_{\text{Br}} + 1)[Br^-] + (3Z_{\text{Br}} + 1)[Br_3^-] + 2Z_{\text{Br}}[Br_2] + (Z_{\text{Br}} - 1)([HBrO] + [BrO^-]) \\ & + (Z_{\text{Br}} - 5)([HBrO_3] + [BrO_3^-]) \\ & + (2Z_{\text{I}} + Z_{\text{Cl}} + 1)[I_2Cl^-] + (Z_{\text{I}} + Z_{\text{Cl}})[ICl] + (Z_{\text{I}} + 2Z_{\text{Cl}} + 1)[ICl_2^-] + (Z_{\text{I}} + Z_{\text{Br}})[IBr] + (Z_{\text{I}} + 2Z_{\text{Br}} + 1)[IBr_2^-] \\ & = (Z_{\text{Br}}C_0V_0 + Z_{\text{Cl}}C_{01}V_0 + 2Z_{\text{I}}CV + Z_{\text{I}}C_1V) / (V_0 + V) \end{aligned} \quad (18)$$

The balance (18) is equivalent to the balance (13).

A remark is needed in relation to the charge balance. Rewriting Equation (8) in terms of concentrations (see

Equation (12)), we have

$$\begin{aligned} & [\text{H}^+] - [\text{OH}^-] + [\text{K}^+] - [\text{I}^-] - [\text{I}_3^-] + [\text{IO}^-] - [\text{IO}_3^-] - [\text{H}_4\text{IO}_6^-] - 2[\text{H}_3\text{IO}_6^{2-}] - [\text{Cl}^-] - [\text{ClO}^-] \\ & - [\text{ClO}_2^-] - [\text{ClO}_3^-] - [\text{ClO}_4^-] - [\text{Br}^-] - [\text{Br}_3^-] - [\text{BrO}^-] - [\text{BrO}_3^-] - [\text{I}_2\text{Cl}^-] - [\text{ICl}_2^-] - [\text{IBr}_2^-] \\ & - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] + [\text{CH}_3\text{OH}_2^+] - [\text{CH}_3\text{O}^-] + [\text{C}_2\text{H}_5\text{OH}_2^+] - [\text{C}_2\text{H}_5\text{O}^-] = 0 \end{aligned} \quad (19)$$

As we see, Equation (19) involves the ionic species related to amphiprotic co-solvents. However, in accordance with the remarks presented in [5], the solvates of pairs of ions: $(\text{CH}_3\text{OH}_2^+, \text{CH}_3\text{O}^-)$ and $(\text{C}_2\text{H}_5\text{OH}_2^+, \text{C}_2\text{H}_5\text{O}^-)$ can be perceived as pairs of solvates of H^+ and OH^- ions.

3. Final Comments

The complex redox system in a mixture with five solvents is considered. The discussion can be extended on mixtures with S solvents, A_1, \dots, A_S , where at least one of the co-solvents has amphiprotic properties. In such systems, the solvates $X_i^{z_i} \cdot n_{iA_1} \dots n_{iA_S}$ are considered/admitted, where $n_{iA_j} \geq 0$ ($j = 1, \dots, S$); Equation (13) is the simplest/shortest form of GEB obtained for the redox system considered according to Approach II to GEB.

Equation (13) was obtained from linear combination of the related balance $2 \cdot f(\text{O}) - f(\text{H})$ (Equation (3)) with: charge balance (Equation (8)), elemental balances for other “fans” (C, K) (Equations (9), (10)), and core balances (Equations (4) - (7)) related to organic solvents in this system. This GEB does not involve the species composed only of “fans”: H, O, C, K. In particular, it does not contain the components explicitly related to the solvent species. The paper is an illustration of the compact formulation of redox systems according to GATES/GEB Principles, presented in Ref. [5].

One can notice that uncharged (neutral) species: I_2 , $\text{I}_{2(s)}$, Cl_2 , Br_2 , ICl , IBr are not present in Equation (13). Note also that Cl^- , Br^- , I^- , Cl_2 , Br_2 , I_2 , $\text{I}_{2(s)}$, Br_3^- , I_3^- , I_2Cl^- , ICl , ICl_2^- , IBr , and IBr_2^- are the species composed only of “players”. In other species, “players” are associated with “fans”, e.g. in HIO_3 (I—“player”; H, O—“fans”).

Note that—at the start—the Approach II does not distinguish between “fans” and “players”; the terms “fans” and “players” are used here only for the needs of the Approach I to GEB. In further parts of this text, the “players” (the electro-active elements) are distinguished later only to indicate the equivalency of the Approaches I and II.

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