A General Property Differentiating Between Redox and Non-Redox Electrolytic Systems and Its Consequences

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ABSTRACT: *The general property of electrolytic systems with aqueous solutions is presented. For this purpose, the linear combination $2 \cdot f(O) – f(H)$ of elemental balances: $f(H)$ for hydrogen (H) and $f(O)$ for oxygen (O) is put in context with other elemental or core balances $f(Y_m)$ $(Y_m \neq H, O)$, and charge balance (ChB) related to the system in question. It is stated that $2 \cdot f(O) – f(H)$ is (a) linearly independent on $f(Y_m)$ and ChB for a redox system, or (b) is linearly dependent on ChB and $f(Y_m)$ when related to a non-redox system. The general manner of formation of the intended/desired linear combination is indicated. The balance $2 \cdot f(O) – f(H)$ is the primary form of the generalized electron balance (GEB), completing the set of equations needed for quantitative description of electrolytic redox systems, $pr\text{-}GEB = 2 \cdot f(O) – f(H)$, according to principles of the generalized approach to electrolytic systems (GATES). The GEB is perceived as a Law of Nature, as the hidden connection of physicochemical laws. 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. These properties can be generalized on non-redox and redox systems of any degree of complexity, also in mixed-solvent media, with amphiprotic co-solvent(s) involved.*
Keywords: GATES, GEB, GATES/GEB, linear combination.

I.   INTRODUCTION

Any electrolytic system is perceived as the macroscopic part of the Universe, selected for observation and experimentation. For modeling purposes, we assume a closed system, separated from its environment/surroundings by diathermal walls, preventing the matter exchange but allowing the exchange of heat, resulting from exo- or endothermic process occurred in the system. This way, any dynamic process, represented by titration, may proceed – for modeling purposes – in *quasistatic* manner, under isothermal conditions. Constant temperature is one of conditions securing constancy of equilibrium constants related to the system in question. In further discussion, we refer to chemical entities with defined chemical composition, formed from the elements, whose atoms/nuclei do not subject to radioactive $(\alpha, \beta^-, \beta^+, $ electron capture) transformations. These entities are considered (*i*) as components/compounds forming a system, or (*ii*) as the species formed in the system/mixture, after mixing these components.

Static and dynamic systems are distinguished. A static system, of volume V_0 mL, is obtained after a disposable mixing specific chemical compounds. A dynamic system can be realized according to titrimetric mode, where V mL of titrant T, added in successive portions into V_0 mL of titrand D, and V_0+V mL of D+T mixture is obtained at this point of the titration, if the assumption of the volumes additivity is valid; D and T are the sub-systems of the D+T system.

In order to balance an electrolytic system, two physical laws of conservation are applied, namely:

$1°$ the law of charge conservation, represented by charge balance ($f_0 = $ ChB), interrelating the numbers N_i of a subset of charged species (ions of i-th kind, $z_i \neq 0$) in the system, and

$2°$ the law of elements/cores conservation, interrelating – in elemental/core balances $f_j = f(Y_j)$ – the numbers N_{0j} of molecules of j-th kind as components forming a system, and the numbers N_i of species of i-th kind formed in the system.

In our considerations we concern the linear dependency or independency of algebraic equations, expressed by charge (ChB) and elemental or core balances, related to the system in question. A core is a cluster of atoms with defined chemical formula, structure and external charge that is not changed in the system; e.g. SO_4^{-2} is a core in Eqs. 16, 22, 30, 41.

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The discussion will concern here aqueous solutions, where 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 = Faraday's constant, N_A = Avogadro's number), $n_i = n_{iW} \geq 0$ is a mean number of water (W=H_2O) molecules attached to $X_i^{z_i}$. For ordering purposes we assume: $X_1^{z_1} = H_2O$, $X_2^{z_2} \cdot n_{2W} = H^{+1} \cdot n_{2W}$, $X_3^{z_3} \cdot n_{3W} = OH^{-1} \cdot n_{3W}, \ldots$, i.e., $z_1 = 0$, $z_2 = 1$, $z_3 = -1, \ldots$. Molar concentration [mol/L] of the species $X_i^{z_i} \cdot n_{iW}$ (i=2,3,...) will be denoted as $[X_i^{z_i}]$. The $n_i = n_{iW}$ values are virtually unknown – even for $X_2^{z_2} = H^{+1}$ [1] in aqueous media, and depend on ionic strength of the solution.

The $X_i^{z_i}$'s with different numbers of H_2O molecules attached, e.g. H^{+1}, H_3O^{+1} and $H_9O_4^{+1}$; $H_4IO_6^{-1}$ and IO_4^{-1}, are considered equivalently, i.e., as the same species, in this medium [2-9].

In further parts of the paper we apply the notations:

o J – number of kinds of components forming the system; $N_0 = [N_{01},\ldots, N_{0j},\ldots, N_{0J}]^T$ – vector of numbers of the components; the main component in aqueous media is water W=H_2O;

o I – number of different kinds of species formed in the system; $N = [N_1,\ldots, N_i,\ldots, N_I]^T$ – vector of numbers of the species, where: N_1 – number of free W=H_2O molecules; N_2 – number of $H^{+1} \cdot n_{2W}$ ions; N_3 – number of $OH^{-1} \cdot n_{3W}$ ions, ...;

o $f_g = f(Y_g)$ – notation of elemental or core balances, expressed in terms of numbers of particular entities: N_{0j} for components, and N_i for species. In particular, we have: $f_1 = f(H)$ for $Y_1 = H$, $f_2 = f(O)$ for $Y_2 = O$; $f_g = f(Y_g)$ ($g \geq 3,\ldots,G$ for $Y_g \neq$ H, O) refer to other elements and/or cores; N_1, together with n_{iW}, are included in the balances $f_1 = f(H)$ and $f_2 = f(O)$;

o $F_g = F(Y_g)$ – notation of elemental or core balances, expressed in terms of molar concentrations; in particular, we have: $F_1 = F(H)$ for $Y_1 = H$, $F_2 = F(O)$ for $Y_2 = O$; $F_g = F(Y_g)$ ($g \geq 3,\ldots,G$ for $Y_g \neq$ H, O) refer to other elements and/or cores.

On this basis, the general property distinguishing between redox and non-redox systems, obligatory for electrolytic systems of any degree of complexity, will be derived, and the generalized electron balance (GEB), completing the set of algebraic equations necessary for quantitative description of redox systems, will be formulated and applied for resolution of the redox system, according to principles assumed in the Generalized Approach to Electrolytic Systems (GATES) [10]. An important generalization, valid for electrolytic systems of any degree of complexity, will also be done. The considerations/generalization can be extended on multi-solvent media, with amphiprotic co-solvent(s) involved [11].

Let us consider the set of G+1 equations: $f_g(x) = \varphi_g(x) - b_g = 0$, where $g = 0,1,\ldots,G$, $x^T = (x_1,\ldots,x_I)$ – transposed (^{T}) vector x, composed of independent (scalar) variables x_i ($i \in <1, I>$); a_{gi}, $b_g \in \mathcal{R}$ are independent (explicitly) on x. After multiplying the equations by the numbers $\omega_g \in \mathcal{R}$, and addition of the resulting equations, we get the linear combination $\sum_{g=0}^{G} \omega_g \cdot f_g(x) = 0 \iff \sum_{g=0}^{G} \omega_g \cdot \varphi_g(x) = \sum_{g=0}^{G} \omega_g \cdot b_g$ of the basic equations.

Formation of linear combinations is applicable to check the linear dependency or independency of the balances. 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, $0 = 0$ [2]. For this purpose we will try, in all instances, to obtain the simplest form of the linear combination. To facilitate these operations, carried out by cancellation of the terms on the left and right sides of equations after changing sides of these equations, we apply the equivalent forms of the starting equations $f_g(x) = 0$:

$f_g(x)$: $\quad \varphi_g(x) - b_g = 0 \iff \varphi_g(x) = b_g \iff \quad - f_g(x)$: $\quad -\varphi_g(x) = -b_g \iff b_g = \varphi_g(x)$

In this notation, $f_g(x)$ will be essentially treated not as the algebraic expression on the left side of the equation $f_g(x) = 0$, but as an equation that can be expressed in alternative forms presented above.

II. LINEAR COMBINATION OF ALGEBRAIC EQUATIONS

Any algebraic equation, and linear equation in particular, can be presented as $f(x) = 0$, where x is a vector of independent variables x_i, $x = [x_1,\ldots,x_I]^T$, where ^{T} is the transposition sign. In turn, for a system of equations $f_g(x) = 0$ ($g = 1,\ldots,G$), after multiplication of each of these equations by the numbers ω_g ($g = 1,\ldots,G$), we get the linear combination thereof

$$\sum_{g=1}^{G} \omega_g \cdot f_g(x) = 0 \tag{1}$$

At properly selected ω_g values, Eq. 1 assumes the simplest form. For the system of linearly dependent equations $f_g(x) = 0$ ($g = 1,\ldots,G$), the simplest linear combination (1) is expressed by the identity, $0 = 0$.

For a beginning, let us consider a set of G linear, algebraic equations

$$\sum_{i=1}^{I} a_{gi} \cdot x_i = b_g \quad \Leftrightarrow \quad \sum_{i=1}^{I} a_{gi} \cdot x_i - b_g = 0 \qquad (g = 1,\ldots,G) \tag{2}$$

where a_{ig} are the coefficients, and b_g – free terms. When multiplying Eq. 2 by ω_g, after subsequent summation we have

$$\sum_{g=1}^{G} \omega_g \cdot \sum_{i=1}^{I} a_{gi} \cdot x_i = \sum_{j=1}^{I} \omega_g \cdot b_g \quad \Leftrightarrow \quad \sum_{i=1}^{I} x_i \cdot \sum_{g=1}^{G} \omega_g \cdot a_{gi} = \sum_{g=1}^{G} \omega_g \cdot b_g \tag{3}$$

Assuming

$$b_g = \sum_{j=1}^{J} b_{gj} \cdot x_{0j} \tag{4}$$

from Eqs. 3 and 4 we have

$$\sum_{i=1}^{I} x_i \cdot \sum_{g=1}^{G} \omega_g \cdot a_{gi} = \sum_{j=1}^{J} x_{0j} \cdot \sum_{g=1}^{G} \omega_g \cdot b_{gj} \tag{5}$$

III. LINEAR COMBINATION OF BALANCES FOR ELECTROLYTIC SYSTEMS

Non-redox and redox electrolytic systems can be formulated with use of charge and elemental or core balances. For some reasons, it is more convenient to start the balancing from the numbers N_{0j} of particular components of the system and the numbers N_i of the species in the system thus formed, and then recalculate them in terms of molar concentrations. This recalculation is needed because the algebraic formulas for equilibrium constants related to electrolytic systems are expressed in terms of molar concentrations.

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Referring to the problem in question, and placing $x_i = N_i$, $x_{0j} = N_{0j}$ in Eqs. 4, 5, we have:

$$b_g = \sum_{j=1}^{J} b_{gj} \cdot N_{0j} \tag{4a}$$

$$\sum_{i=1}^{I} N_i \cdot \sum_{g=1}^{G} \omega_g \cdot a_{gi} = \sum_{j=1}^{J} N_{0j} \cdot \sum_{g=1}^{G} \omega_g \cdot b_{gj} \tag{5a}$$

The charge balance: $f_0 = $ ChB and $F_0 = $ CHB, is expressed as follows

$$(a) \ ChB: \ f_0 = \sum_{i=2}^{I} a_{0i} \cdot N_i = \sum_{i=2}^{I} z_i \cdot N_i = 0 \ ; \ (b) \ CHB: \ F_0 = \sum_{i=2}^{I} z_i \cdot [X_i^{z_i}] = 0 \tag{6}$$

where $a_{0i} = z_i$, and :

$$[X_i^{z_i}] = 10^3 \cdot N_i / N_A / V_0 \tag{7}$$

in a static, or

$$[X_i^{z_i}] = 10^3 \cdot N_i / N_A / (V_0 + V) \tag{8}$$

in a dynamic system; $z_1 = 0$ for $X_1^{z_1} = H_2O$, $z_2 = +1$ for $X_2^{z_2} = H^{+1}$, $z_3 = -1$ for $X_3^{z_3} = OH^{-1}$, … .

For ChB (g=0), where the right side equals zero, from Eq, 4a we have:

$$b_0 = \sum_{j=1}^{J} b_{0j} \cdot N_{0j} = 0 \quad \Rightarrow \quad b_{0j} = 0 \ (j=1,\ldots,J) \tag{4b}$$

and Eq. 5a can be completed as follows

$$\sum_{i=1}^{I} N_i \cdot \sum_{g=0}^{G} \omega_g \cdot a_{gi} = \sum_{j=1}^{J} N_{0j} \cdot \sum_{g=0}^{G} \omega_g \cdot b_{gj} \tag{5b}$$

The elemental/core balances: $f(H)$, $f(O)$ and $f(Y_g)$ ($Y_g \neq$ H, O, g≥3,…,G) are written as follows:

$$f_1 = f(H) = \sum_{i=1}^{I} (a_{1i} + 2n_{iW}) \cdot N_i - \sum_{j=1}^{J} b_{1j} \cdot N_{0j} = 0 \ \text{for} \ Y_1 = H, \ f_2 = f(O) = \sum_{i=1}^{I} (a_{2i} + n_{iW}) \cdot N_i - \sum_{j=1}^{J} b_{2j} \cdot N_{0j} = 0 \ \text{for}$$

$$Y_2 = O, \ldots , \ f_g = \sum_{i=1}^{I} a_{gi} \cdot N_i - \sum_{j=1}^{J} b_{gj} \cdot N_{0j} = 0 , \ldots, \ f_G = \sum_{i=1}^{I} a_{Gi} \cdot N_i - \sum_{j=1}^{J} b_{Gj} \cdot N_{0j} = 0 \tag{9}$$

where a_{gi} and b_{gj} are the numbers of atoms/cores of g-th kind in i-th species and j-th component, resp. Then the balance

$$f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(O) - f(H) = \sum_{i=2}^{I} (2a_{2i} - a_{1i}) \cdot N_i - \sum_{j=1}^{J} (2b_{2j} - b_{1j}) \cdot N_{0j} = 0 \tag{10}$$

is formulated. Denoting, for a moment, $\omega_1 = -1$, $\omega_2 = 2$, we transform the balance (10) into the form

$$f_{12} = \omega_1 \cdot (\sum_{i=2}^{I} (a_{1i} \cdot N_i - \sum_{j=1}^{J} b_{2j} \cdot N_{0j}) + \omega_2 \cdot (\sum_{i=2}^{I} (a_{2i} \cdot N_i - \sum_{j=1}^{J} (b_{2j} \cdot N_{0j}) = \omega_1 \cdot f_1^* + \omega_2 \cdot f_2^* = 0 \tag{10a}$$

In Equation 10a, the expressions for f_1^* and f_2^* have the shape similar to the general expression for f_g (g=3,...,G) in Eqs. 9.

In the balances related to aqueous media, the terms involved with water, namely N_1, N_{0j} (for j related to H_2O, as the component), and all $n_i = n_{iW}$ are not involved in $f_0, f_3, ..., f_G$, or are cancelled within f_{12}, Eqs. 10, 10a). The species in which H and O are not involved in $X_i^{z_i}$, are also cancelled within f_{12}. Also the entities $X_i^{z_i}$ that can be rewritten into the form $(H_2O)_m U_i^{z_i}$ (m=0,1,...), with a sub-core $U_i^{z_i}$, where H and O are not involved, are cancelled within f_{12} (Eq. 10); e.g. CH_3COOH, as components and species, is transformable (mentally, purposefully) into $C_2H_4O_2 \equiv C_2(H_2O)_2$. As will be stated later, the ω_g values are involved with excessive H and/or O atoms within the sub-core $U_i^{z_i}$ of $X_i^{z_i} = (H_2O)_m U_i^{z_i}$.

For the convenience of linear combination of f_{12} with other elemental/core balances, we can apply the equivalent relations for $g \geq 3,...,G$:

$$f_g = \sum_{i=1}^{I} a_{gi} \cdot N_i - \sum_{j=1}^{J} b_{gj} \cdot N_{0j} = 0 \qquad \Leftrightarrow \qquad \sum_{i=1}^{I} a_{gi} \cdot N_i = \sum_{j=1}^{J} b_{gj} \cdot N_{0j} \tag{11}$$

for a positive oxidation degree, or

$$-f_g = \sum_{j=1}^{J} b_{gj} \cdot N_{0j} - \sum_{i=1}^{I} a_{gi} \cdot N_i = 0 \qquad \Leftrightarrow \qquad \sum_{j=1}^{J} b_{gj} \cdot N_{0j} = \sum_{i=1}^{I} a_{gi} \cdot N_i \tag{12}$$

for a negative oxidation degree.

The linear combination of all G balances: $f_0, f_{1,2}, f_3, ..., f_G$, obtained from Eqs. 5a and 6a, can be presented in equivalent forms:

$$\sum_{i=1}^{I} N_i \cdot \left(z_i + \sum_{g=1}^{G} \omega_g \cdot a_{gi} \right) = \sum_{j=1}^{J} N_{0j} \cdot \sum_{g=1}^{G} \omega_g \cdot b_{gj} \tag{13a}$$

$$\sum_{i=1}^{I} N_i \cdot z_i + \sum_{g=1}^{G} \omega_g \cdot \left(\sum_{i=1}^{I} N_i \cdot a_{gi} - \sum_{j=1}^{J} N_{0j} \cdot b_{gj} \right) = 0 \tag{13b}$$

$$f_0 + f_{12} + \sum_{g=3}^{G} \omega_g \cdot f_g = 0 \tag{13c}$$

$$ChB + (2 \cdot f(O) - f(H)) + \sum_{g=3}^{G} \omega_g \cdot f(Y_i) = 0 \tag{13d}$$

$$(+1) \cdot f(H)) + (-2) \cdot f(O) + \sum_{g=3}^{G} (-\omega_g) \cdot f(Y_i) - ChB = 0 \tag{13e}$$

All multipliers at N_i and N_{0j} in Eq. 13a are cancelled simultaneously if we have:

$$z_i + \sum_{g=1}^{G} \omega_g \cdot a_{gi} = 0 \text{ and } \sum_{g=1}^{G} \omega_g \cdot b_{gj} = 0 \tag{14}$$

for all i and j values (i = 1,...,I; j = 1,...,J), i.e., Eq. 13a is transformed into identity

$$\sum_{i=1}^{I} N_i \cdot 0 = \sum_{j=1}^{J} N_{0j} \cdot 0 \qquad \Leftrightarrow \qquad 0 = 0 \tag{15}$$

Transformation of a set of the equations into the identity, 0 = 0, proves the linear dependence between the equations considered [2]. Then from Equation 13c we have

$$f_{12} = \sum_{g=3}^{G} (-\omega_g) \cdot f_g - f_0 \tag{13f}$$

i.e., f_{12} is the dependent balance.

IV. A NON-REDOX SYSTEM

We refer here to titration of V_0 mL of the titrand D composed of $ZnSO_4$ (C_0) + NH_3 (C_{01}) + NH_4Cl (C_{02}) + erio T = $C_{20}H_{12}N_3O_7SNa$ (C_{03}) with V mL of EDTA (C) as titrant T [12] added up to a given point of the titration. We assume that V_0 mL of D is composed of N_{01} molecules of $ZnSO_4 \cdot 7H_2O$, N_{02} molecules of NH_3, N_{03} molecules of NH_4Cl, N_{04} molecules of $NaH_2In = C_{20}H_{12}N_3O_7SNa$, N_{05} molecules of H_2O, and V mL of titrant T is composed of: N_{06} molecules of EDTA = $Na_2H_2L \cdot 2H_2O = C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$ and N_{07} molecules of H_2O. In V_0+V mL of the D+T mixture thus formed, we have the following 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), Cl^{-1} (N_6,n_6), Na^{+1} (N_7,n_7), NH_4^{+1} (n_8,N_8), NH_3 (n_9,N_9), Zn^{+2} (N_{10},n_{10}), $ZnOH^{+1}$ (N_{11},n_{11}), soluble complex $Zn(OH)_2$ (N_{12},n_{12}), $Zn(OH)_3^{-1}$ (N_{13},n_{13}), $Zn(OH)_4^{-2}$ (N_{14},n_{14}), $ZnNH_3^{+2}$ (N_{15},n_{15}), $Zn(NH_3)_2^{+2}$ (N_{16},n_{16}), $Zn(NH_3)_3^{+2}$ (N_{17},n_{17}), $Zn(NH_3)_4^{+2}$ (N_{18},n_{18}), $ZnCl^{+1}$ (N_{19},n_{19}), $ZnSO_4$ (N_{20},n_{20}), $C_{20}H_{13}N_3O_7S$ (N_{21},n_{21}), $C_{20}H_{12}N_3O_7S^{-1}$ (N_{22},n_{22}), $C_{20}H_{11}N_3O_7S^{-2}$ (N_{23},n_{23}), $C_{20}H_{10}N_3O_7S^{-3}$ (N_{24},n_{24}), $C_{20}H_{10}N_3O_7SZn^{-1}$ (N_{25},n_{25}), $(C_{20}H_{10}N_3O_7S)_2Zn^{-4}$ (N_{26},n_{26}), $C_{10}H_{18}N_2O_8^{+2}$ (H_6L^{+2}) (N_{27},n_{27}), $C_{10}H_{17}N_2O_8^{+1}$ (H_5L^{+1}) (N_{28},n_{28}), $C_{10}H_{16}N_2O_8$ (H_4L) (N_{29},n_{29}), $C_{10}H_{15}N_2O_8^{-1}$ (H_3L^{-1}) (N_{30},n_{30}), $C_{10}H_{14}N_2O_8^{2-}$ (H_2L^{-2}) (N_{31},n_{31}), $C_{10}H_{13}N_2O_8^{-3}$ (HL^{-3}) (N_{32},n_{32}), $C_{10}H_{12}N_2O_8^{-4}$ (L^{-4}) (N_{33},n_{33}), $C_{10}H_{13}N_2O_8Zn^{-1}$ ($ZnHL^{-1}$) (N_{34},n_{34}), $C_{10}H_{12}N_2O_8Zn^{-2}$ (ZnL^{-2}) (N_{35},n_{35}), $C_{10}H_{13}N_2O_9Zn^{-3}$ ($ZnOHL^{-3}$) (N_{36},n_{36}).

These species are arranged in the following balances:

$f_1 = f(H)$:

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + 2N_6n_6 + 2N_7n_7 + N_8(4+2n_8) + N_9(3+2n_9) + 2N_{10}n_{10}$
$+ N_{11}(1+2n_{11}) + N_{12}(2+2n_{12}) + N_{13}(3+2n_{13}) + N_{14}(4+2n_{14}) + N_{15}(3+2n_{15}) + N_{16}(6+2n_{16}) + N_{17}(9+2n_{17})$
$+ N_{18}(12+2n_{18}) + 2N_{19}n_{19} + 2N_{20}n_{20} + N_{21}(13+2n_{21}) + N_{22}(12+2n_{22}) + N_{23}(11+2n_{23}) + N_{24}(10+2n_{24})$
$+ N_{25}(10+2n_{25}) + N_{26}(20+2n_{26}) + N_{27}(18+2n_{27}) + N_{28}(17+2n_{28}) + N_{29}(16+2n_{29}) + N_{30}(15+2n_{30})$
$+ N_{31}(14+2n_{31}) + N_{32}(13+2n_{32}) + N_{33}(12+2n_{33}) + N_{34}(13+2n_{34}) + N_{35}(12+2n_{35}) + N_{36}(13+2n_{36})$
$= 14N_{01} + 3N_{02} + 4N_{03} + 12N_{04} + 2N_{05} + 18N_{06} + 2N_{07}$

$f_2 = f(O)$:

$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6n_6 + N_7n_7 + N_8n_8 + N_9n_9 + N_{10}n_{10}$
$+ N_{11}(1+n_{11}) + N_{12}(2+n_{12}) + N_{13}(3+n_{13}) + N_{14}(4+n_{14}) + N_{15}n_{15} + N_{16}n_{16} + N_{17}n_{17}$
$+ N_{18}n_{18} + N_{19}n_{19} + N_{20}(4+n_{20}) + N_{21}(7+n_{21}) + N_{22}(7+n_{22}) + N_{23}(7+n_{23}) + N_{24}(7+n_{24})$
$+ N_{25}(7+n_{25}) + N_{26}(14+n_{26}) + N_{27}(8+n_{27}) + N_{28}(8+n_{28}) + N_{29}(8+n_{29}) + N_{30}(8+n_{30})$
$+ N_{31}(8+n_{31}) + N_{32}(8+n_{32}) + N_{33}(8+n_{33}) + N_{34}(8+n_{34}) + N_{35}(8+n_{35}) + N_{36}(9+n_{36})$
$= 11N_{01} + 7N_{04} + N_{05} + 10N_{06} + N_{07}$

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

$- N_2 + N_3 + 7N_4 + 8N_5 - 4N_8 - 3N_9 + N_{11} + 2N_{12} + 3N_{13} + 4N_{14} - 3N_{15} - 6N_{16} - 9N_{17} - 12N_{18} + 8N_{20} + N_{21}$
$+ 2N_{22} + 3N_{23} + 4N_{24} + 4N_{25} + 8N_{26} - 2N_{27} - N_{31} + N_{30} + 2N_{31} + 3N_{32} + 4N_{33} + 3N_{34} + 4N_{35} + 5N_{36}$
$= 8N_{01} - 3N_{02} - 4N_{03} + 2N_{04} + 2N_{06}$ (16)

$f_0 = ChB$

$N_2 - N_3 - N_4 - 2N_5 - N_6 + N_7 + N_8 + 2N_{10} + N_{11} - N_{13} - 2N_{14} + 2N_{15} + 2N_{16} + 2N_{17} + 2N_{18} + N_{19} - N_{22} - 2N_{23}$
$- 3N_{24} - N_{25} - 4N_{26} + 2N_{27} + N_{28} - N_{30} - 2N_{31} - 3N_{32} - 4N_{33} - N_{34} - 2N_{35} - 3N_{36} = 0$ (17)

$f_3 = f(Cl)$: $N_6 + N_{21} = N_{03}$ (18)

$-f_4 = -f(Na)$: $N_{04} + 2N_{06} = N_7$ (19)

$-f_5 = -f(S) = -f(SO_4)$: $N_{01} = N_4 + N_5 + N_{20}$ (20)

$f_6 = f(NH_3)$: $N_8 + N_9 + N_{16} + 2N_{17} + 3N_{18} + 4N_{19} = N_{02} + N_{03}$ (21)

$-f_7 = -f(Zn)$:

$N_{01} = N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + N_{15} + N_{16} + N_{17} + N_{18} + N_{19} + N_{20} + N_{21} + N_{22} + N_{34} + N_{35} + N_{36}$ (22)

$-f_8 = -f(C_{20}H_{12}N_3O_7S)$: $N_{04} = N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + 2N_{26}$ (23)

$f_9 = f(C_{10}H_{12}N_2O_8)$

$N_{27} + N_{28} + N_{29} + N_{30} + N_{31} + N_{32} + N_{33} + N_{34} + N_{35} + N_{36} = N_{06}$ (24)

Then we have, by turns,

$2 \cdot f(O) - f(H) + ChB + f(Cl) - f(Na) - 6 \cdot f(SO_4) + 3 \cdot f(NH_3) - 2 \cdot f(Zn) - f(C_{20}H_{10}N_3O_7S)$
$- 0 \cdot f(C_{10}H_{12}N_2O_8) = 0$ (25)

$(+1) \cdot f(H) + (-2) \cdot f(O) + (-1) \cdot f(Cl) + (+1) \cdot f(Na) + (+6) \cdot f(SO_4) + (-3) \cdot f(NH_3) + (+2) \cdot f(Zn) + (+1) \cdot f(C_{20}H_{10}N_3O_7S)$
$+ 0 \cdot f(C_{10}H_{12}N_2O_8) - ChB = 0$ (26)

$2 \cdot f(O) - f(H) = -f(Cl) + f(Na) + 6 \cdot f(SO_4) - 3 \cdot f(NH_3) + 2 \cdot f(Zn) + f(C_{20}H_{10}N_3O_7S) - ChB$

Because all the components N_i and N_{0i} in Eq. 25 are cancelled, it follows that Eq. 25 and then Eq. 26 express the identity, $0 = 0$. From Eq. 26 we see that the multipliers of the corresponding simple ions are equal to their oxidation numbers: $\omega_1 = +1$ for H, $\omega_2 = -2$ for O, $\omega_3 = -1$ for Cl, $\omega_4 = +1$ for Na, $\omega_7 = +2$ for Zn. The multipliers for $f(SO_4)$ and $f(NH_3)$ are equal to oxidation numbers: $\omega_5 = +6$ for S in SO_4^{-2}, and $\omega_6 = -3$ for N in NH_3. As refers to $H_3In = C_{20}H_{13}N_3O_7S = C_{20}N_3S(H_2O)_6OH$, we have $x=\omega_8 = 1$, calculated from $x-2+1 = 0$, whereas for $H_4L = C_{10}H_{16}N_2O_8 = C_{10}N_2(H_2O)_8$ we have $\omega_9 = 0$.

The element S enters the balance (20) as a core SO_4^{-2}; note that S enters also another core in Eq. 23. Moreover, N enters different cores in Eqs. 21, 23 and 24. Each of the relations: 18, 19, involving only one kind of species, is considered as equality, not equation. In equations we have at least two kinds of species, interrelated in expression(s) for the corresponding equilibrium constant(s). In an equality, concentration of the species is a number at defined volume V considered, from the calculation viewpoint, as a parameter of the related system. This remark is put in context with the equality of the numbers of equations and the numbers of; we have there CHB and 5 concentration balances and 6 independent variables composing the vector $\mathbf{x}$ = (pH, pSO$_4$, pNH$_3$, pZn, pC$_{10}$H$_{12}$N$_2$O$_8$, pC$_{10}$H$_{12}$N$_2$O$_8$)^T, where pX$_i$ = -log[X$_i$]. The CHB and CB(Y$_g$) are obtained on the basis of Eqs. 17, 20 – 24 and the relations: (8), $C_0V_0 = 10^3 \cdot N_{01}/N_A$, $C_{01}V_0 = 10^3 \cdot N_{02}/N_A$, $C_{02}V_0 = 10^3 \cdot N_{03}/N_A$, $C_{03}V_0 = 10^3 \cdot N_{04}/N_A$, $CV = 10^3 \cdot N_{06}/N_A$.

Because $2 \cdot f(O) - f(H)$ (Eq. 16) is not an independent balance, the balances: $f(O)$ and $f(H)$ and then $f(O) - f(H)$ are not formulated in mathematical description of this (non-redox) system. This regularity is obligatory for all non-redox systems, of any degree of complexity.

V.   A REDOX SYSTEM

We refer here to titration of V_0 mL of the titrand D containing FeSO$_4$ (C$_0$) + H$_2$SO$_4$ (C$_{01}$) with V mL of titrant T, containing KMnO$_4$ (C) , added up to a given point of the titration. We assume that V_0 mL of D is composed of FeSO$_4\cdot$7H$_2$O (N$_{01}$ molecules), H$_2$SO$_4$ (N$_{02}$ molecules) and H$_2$O (N$_{03}$ molecules), and V mL of T is composed of KMnO$_4$ (N$_{04}$ molecules), and H$_2$O (N$_{05}$ molecules). In V_0+V mL of the D+T mixture thus formed we have the following species: H$_2$O (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$_5$), Fe^{+2} (N$_6$,n$_6$), FeOH^{+1} (N$_7$,n$_7$), FeSO$_4$ (N$_8$,n$_8$), Fe^{+3} (N$_9$, n$_9$), FeOH^{+2} (N$_{10}$, n$_{10}$), Fe(OH)$_2^{+1}$ (N$_{11}$, n$_{11}$), Fe$_2$(OH)$_2^{+4}$ (N$_{12}$, n$_{12}$), FeSO$_4^{+1}$ (N$_{13}$, n$_{13}$), Fe(SO$_4$)$_2^{-1}$ (N$_{14}$, n$_{14}$), Mn^{+2} (N$_{15}$, n$_{15}$), MnOH^{+1} (N$_{16}$, n$_{16}$), MnSO$_4$ (N$_{17}$, n$_{17}$), Mn^{+3} (N$_{18}$, n$_{18}$), MnOH^{+2} (N$_{19}$, n$_{19}$), MnO$_4^{-2}$ (N$_{20}$, n$_{20}$), MnO$_4^{-1}$ (N$_{21}$, n$_{21}$), K^{+1} (N$_{22}$, n$_{22}$).

The balances for this system are as follows:

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + 2N_6n_6 + N_7(1+2n_7) + 2N_8n_8 + 2N_9n_9 + N_{10}(1+2n_{10})$
$+ N_{11}(2+2n_{11}) + N_{12}(2+2n_{12}) + 2N_{13}n_{13} + 2N_{14}n_{14} + 2N_{15}n_{15} + N_{16}(1+2n_{16}) + 2N_{17}n_{17} + 2N_{18}n_{18} + N_{19}(1+2n_{19})$
$+ 2N_{20}n_{20} + 2N_{21}n_{21} + 2N_{22}n_{22} = 14N_{01} + 2N_{02} + 2N_{03} + 2N_{05}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6n_6 + N_7(1+n_7) + N_8(4+n_8) + N_9n_9 + N_{10}(1+n_{10}) + N_{11}(2+n_{11})$
$+ N_{12}(2+n_{12}) + N_{13}(4+n_{13}) + N_{14}(8+n_{14}) + N_{15}n_{15} + N_{16}(1+n_{16}) + N_{17}(4+n_{17}) + N_{18}n_{18} + N_{19}(1+n_{19}) + N_{20}(4+n_{20})$
$+ N_{21}(4+n_{21}) + N_{22}n_{22} = 11N_{01} + 4N_{02} + N_{03} + 4N_{04} + N_{05}$

$f_0 = ChB$

$N_2 - N_3 - N_4 - 2N_5 + 2N_6 + N_7 + 3N_9 + 2N_{10} + N_{11} + 4N_{12} + N_{13} - N_{14} + 2N_{15} + N_{16} + 3N_{18} + 2N_{19} - 2N_{20} - N_{21}$
$+ N_{22} = 0$ (27)

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

$-N_2 + N_3 + 7N_4 + 8N_5 + N_7 + 8N_8 + N_{10} + 2N_{11} + 2N_{12} + 8N_{13} + 16N_{14} + N_{16} + 8N_{17} + N_{19} + 8N_{20} + 8N_{21}$
$= 8N_{01} + 6N_{02} + 8N_{04}$ (28)

$-f_3 = -f(K) :$ $N_{04} = N_{22}$ (29)

$-f_4 = -f(S) = -f(SO_4) :$ $N_{01} + N_{02} = N_4 + N_5 + N_8 + N_{13} + 2N_{14} + N_{17}$ (30)

$f_5 = f(Fe) :$ $N_6 + N_7 + N_8 + N_9 + N_{10} + N_{11} + 2N_{12} + N_{13} + N_{14} = N_{01}$ (31)

$f_6 = f(Mn) :$ $N_{15} + N_{16} + N_{17} + N_{18} + N_{19} + N_{20} + N_{21} = N_{04}$ (32)

The linear combination, composed from balances for electron-non-active elements ('fans' [2,3]), has the form

$2 \cdot f(O) - f(H) + ChB - f(K) - 6 \cdot f(SO_4) = 0$ (33)

$2(N_6 + N_7 + N_8) + 3(N_9 + N_{10} + N_{11} + 2N_{12} + N_{13} + N_{14}) + 2(N_{15} + N_{16} + N_{17}) + 3(N_{18} + N_{19}) + 6N_{20} + 7N_{21}$
$= 2N_{01} + 7N_{04}$ (33a)

The simplest equation, represented by the balance, involving also electron-active elements ('players') [2]:

$2 \cdot f(O) - f(H) + ChB - f(K) - 6 \cdot f(S) - 3 \cdot f(Fe) - 2 \cdot f(Mn) = 0$ (34)

$(N_{18} + N_{19}) + 4N_{20} + 5N_{21} - (N_6 + N_7 + N_8) = 5N_{04} - N_{01}$ (34a)

is different from identity 0 = 0, Multiplying Eqs. 34 and 34a by –1, we have:

$(+1) \cdot f(K) + (+6) \cdot f(SO_4) + (+3) \cdot f(Fe) + (+2) \cdot f(Mn) + (-2) \cdot f(O) + (+1) \cdot f(H) - ChB = 0$ (35)

$(N_6 + N_7 + N_8) - (5N_{21} + 4N_{20} + N_{18} + N_{19}) = N_{01} - 5N_{04}$ (35a)

Applying the relations: (8) and: $10^3 \cdot N_{01}/N_A = C_0V_0$, $10^3 \cdot N_{04}/N_A = CV$, from Eq. 35a we have [13]

$[Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] - (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}]) = (C_0V_0 - 5CV)/(V_0+V)$ (36)

It is the simplest/shortest form of GEB related to this system, obtained from linear combination of the balances as specified in Eq. 34, where the multipliers applied are equal to the oxidation numbers of the corresponding elements in the species present in this system. i.e. f_{12} (Eq. 28) is not a linear combination of ChB and $f_g = f(Y_g)$, g=3,...,6.

Denoting atomic numbers of Fe and Mn by Z_{Fe} (= 26) and Z_{Mn} (= 25), from Eqs. 31, 32 and 33a we get the balance

$$Z_{Fe} \cdot f(Fe) + Z_{Mn} \cdot f(Mn) - (2 \cdot f(O) - f(H) + ChB + f(K) + 6 \cdot f(S)) = 0 \tag{37}$$

$$(Z_{Fe}-2)(N_6+N_7+N_8) + (Z_{Fe}-3)(N_9+N_{10}+N_{11}+2N_{12}+N_{13}+N_{14}) + (Z_{Mn}-2)(N_{15}+N_{16}+N_{17}) +$$
$$(Z_{Mn}-3)(N_{18}+N_{19}) + (Z_{Mn}-6)N_{20} + (Z_{Mn}-7)N_{21} = (Z_{Fe}-2)N_{01} + (Z_{Mn}-7)N_{04} \tag{37a}$$

Then we have the balance

$$(Z_{Fe}-2)([Fe^{+2}]+[FeOH^{+1}]+[FeSO_4]) + (Z_{Fe}-3)([Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+$$
$$[FeSO_4^{+1}] +[Fe(SO_4)_2^{-1}]) + (Z_{Mn}-2)([Mn^{+2}]+[MnOH^{+1}]+[MnSO_4]) + (Z_{Mn}-3)([Mn^{+3}]+[MnOH^{+2}])$$
$$+ (Z_{Mn}-6)[MnO_4^{-2}] + (Z_{Mn}-7)[MnO_4^{-1}] = (Z_{Fe}-2)C_0V_0 + (Z_{Fe}-7)CV)/(V_0+V) \tag{38}$$

identical with GEB obtained immediately according to Approach I to GEB [13-16].

VI.   CONCLUSIONS

The question of linear dependence or independence of the equations presented in sections 4 and 5 can be summarized as follows. From G+1 starting balances: $f_0, f_1, f_2, f_3, \dots, f_G$ we obtain G balances: $f_0, f_{12}, f_3, \dots, f_G$. If f_{12} is the dependent balance, we have G–1 independent balances: $f_0, f_3, \dots, f_G$; it is the case related to non-redox systems. If f_{12} is the independent balance, we have G independent balances: $f_0, f_{12}, f_3, \dots, f_G$, that will be rearranged – optionally – as the set $(f_{12}, f_0, f_3, \dots, f_G)$ related to GEB, ChB, and $f(Y_g)$ (g=3,…,G), respectively. The number of elemental/core balances $f(Y_g)$ ($Y_g \neq$ H, O, g=3,…,G) and then the number of concentration balances $CB(Y_g)$ in redox systems equals K = G–2.

For redox systems, we have G independent variables, considered as components of the vector $\mathbf{x}$ = (E, pH, pY_3, …, pY_G)^T, where pY_g = –log[Y_g] for g = 3,…,G. Each of the variables is ascribed to particular balance: E – to GEB, pH – to CHB, etc. . For non-redox systems, we have G–1 independent variables, considered as the components of the vector $\mathbf{x}$ = (pH,pY_3,…,pY_G)^T, where pY_g = –log[Y_g] for g = 3,…,G.

One can recall here a more complex redox system, where three electron-active elements (considered in the card-game terminology as 'players') are involved [8]. It is the D+T system, where V mL of T composed of $KMnO_4$ (N_{01} molecules) + CO_2 (N_{02}) + H_2O (N_{03}) is added into V_0 mL of D composed of $FeSO_4 \cdot 7H_2O$ (N_{04}) + $H_2C_2O_4 \cdot 2H_2O$ (N_{05}) + H_2SO_4 (N_{06}) + CO_2 (N_{07}) + H_2O (N_{08}). This system involves the following species:
H_2O (N_1), H^{+1} (N_2,n_2), OH^{-1} (N_3,n_3), K^{+1} (N_4,n_4), HSO_4^{-1} (N_5,n_5), SO_4^{-2} (N_6,n_6), $H_2C_2O_4$ (N_7,n_7), $HC_2O_4^{-1}$ (N_8,n_8), $C_2O_4^{-2}$ (N_9,n_9), H_2CO_3 (N_{10},n_{10}), HCO_3^{-1} (N_{11},n_{11}), CO_3^{-2} (N_{12},n_{12}), MnO_4^{-1} (N_{13},n_{13}), MnO_4^{-2} (N_{14},n_{14}), Mn^{+3} (N_{15},n_{15}), $MnOH^{+2}$ (N_{16},n_{16}), $MnC_2O_4^{+1}$ (N_{17},n_{17}), $Mn(C_2O_4)_2^{-1}$ (N_{18},n_{18}), $Mn(C_2O_4)_3^{-3}$ (N_{19},n_{19}), Mn^{+2} (N_{20},n_{20}), $MnOH^{+1}$ (N_{21},n_{21}), $MnSO_4$ (N_{22},n_{22}), MnC_2O_4 (N_{23},n_{23}), $Mn(C_2O_4)_2^{-2}$ (N_{24},n_{24}), $Mn(C_2O_4)_3^{-4}$ (N_{25},n_{25}), Fe^{2+} (N_{26},n_{26}), $FeOH^{+1}$ (N_{27},n_{27}), $FeSO_4$ (N_{28},n_{28}), $Fe(C_2O_4)_2^{-2}$ (N_{29},n_{29}), $Fe(C_2O_4)_3^{-4}$ (N_{30},n_{30}), Fe^{+3} (N_{31},n_{31}), $FeOH^{+2}$ (N_{32},n_{32}), $Fe(OH)_2^{+1}$ (N_{33},n_{33}), $Fe_2(OH)_2^{+4}$ (N_{34},n_{34}), $FeSO_4^{+1}$ (N_{35},n_{35}), $Fe(SO_4)_2^{-1}$ (N_{36},n_{36}), $FeC_2O_4^{+1}$ (N_{37},n_{37}), $Fe(C_2O_4)_2^{-1}$ (N_{38},n_{38}), $Fe(C_2O_4)_3^{-3}$ (N_{39},n_{39}), **FeC_2O_4** (N_{40},n_{40}), **MnC_2O_4** (N_{41},n_{41}).

In this system we have I = 41 species. Excluding K^{+1} as a not complexing species in this system, we have I–1 = 40. The set of G=6 balances with G=6 independent scalar variables as components of the vector $\mathbf{x}$ = (E, pH, pSO_4, pC_2O_4,pMn2,pFe2)^T, where: E – potential, pH = –log[H^{+1}], pSO_4 = –log[SO_4^{-2}], pC_2O_4 = –log[$C_2O_4^{-2}$], pMn2 =log[Mn^{+2}], pFe2 = –log[Fe^{+2}] is formulated on the basis of balances $f_{12}, f_0, f_3, f_4, f_5, f_6$. The number of equilibrium constants involved in relations for the equilibrium constants (specified below) is 34; then we get 40 = 6+34. The relations are here as follows:

$[OH^{-1}]$ = 10^{pH-14}, $[HSO_4^{-1}]$ = $10^{1.8-pH} \cdot [SO_4^{-2}]$, $[H_2C_2O_4]$ = $10^{5.2-2pH} \cdot [C_2O_4^{-2}]$, $[HC_2O_4^{-1}]$ = $10^{3.8-pH} \cdot [C_2O_4^{-2}]$, $[H_2CO_3]$ = $10^{A(E+0.396)+pH} \cdot [H_2C_2O_4]^{0.5}$, $[H_2CO_3]$ = $10^{16.4-2pH} \cdot [CO_3^{-2}]$, $[HCO_3^{-1}]$ = $10^{10.1-pH} \cdot [CO_3^{-2}]$, $[MnO_4^{-1}]$ = $10^{5A(E-1.507)+8pH} \cdot [Mn^{+2}]$, $[MnO_4^{-2}]$ = $10^{4A(E-1.743)+8pH} \cdot [Mn^{+2}]$, $[Mn^{+3}]$ = $10^{A(E-1.509)} \cdot [Mn^{+2}]$, $[Fe^{+3}]$ = $10^{A(E-0.771)} \cdot [Fe^{+2}]$, K_{sp1} = $[Fe^{+2}][C_2O_4^{-2}]$ (pK_{sp1}=6.7), K_{sp2} = $[Mn^{+2}][C_2O_4^{-2}]$ (pK_{sp2}=5.3), $[FeOH^{+1}]$ = $10^{4.5} \cdot [Fe^{+2}][OH^{-1}]$, $[FeOH^{+2}]$ = $10^{11.0} \cdot [Fe^{+3}][OH^{-1}]$, $[Fe(OH)_2^{+1}]$ = $10^{21.7} \cdot [Fe^{+3}][OH^{-1}]^2$, $[Fe_2(OH)_2^{+4}]$ = $10^{25.1} \cdot [Fe^{+3}]^2[OH^{-1}]^2$, $[MnOH^{+1}]$ = $10^{3.4} \cdot [Mn^{+2}][OH^{-1}]$, $[FeSO_4]$ = $10^{2.3} \cdot [Fe^{+2}][SO_4^{-2}]$, $[FeSO_4^{+1}]$ = $10^{4.18} \cdot [Fe^{+3}][SO_4^{-2}]$, $[Fe(SO_4)_2^{-1}]$ = $10^{7.4} \cdot [Fe^{+3}][SO_4^{-2}]^2$, $[MnSO_4]$ = $10^{2.28} \cdot [Mn^{+2}][SO_4^{-2}]$, $[Fe(C_2O_4)_2^{-2}]$ = $10^{4.52} \cdot [Fe^{+2}][C_2O_4^{-2}]^2$, $[Fe(C_2O_4)_3^{-4}]$ = $10^{5.22} \cdot [Fe^{+2}][C_2O_4^{-2}]^3$, $[FeC_2O_4^{+1}]$ = $10^{7.53} \cdot [Fe^{+3}][C_2O_4^{-2}]$, $[Fe(C_2O_4)_2^{-1}]$ = $10^{13.64} \cdot [Fe^{+3}][C_2O_4^{-2}]^2$, $[Fe(C_2O_4)_2^{-3}]$ = $10^{18.49} \cdot [Fe^{+3}][C_2O_4^{-2}]^3$, $[MnC_2O_4]$ = $10^{3.82} \cdot [Mn^{2+}][C_2O_4^{2-}]$, $[Mn(C_2O_4)_2^{-2}]$ = $10^{5.25} \cdot [Mn^{+2}][C_2O_4^{-2}]^2$, $[MnC_2O_4^{+1}]$ = $10^{9.98} \cdot [Mn^{+3}][C_2O_4^{-2}]$, $[Mn(C_2O_4)_2^{-1}]$ = $10^{16.57} \cdot [Mn^{+3}][C_2O_4^{-2}]^2$, $[Mn(C_2O_4)_3^{-3}]$ = $10^{19.42} \cdot [Mn^{+3}][C_2O_4^{-2}]^3$, where A = F/(R$T$·ln10) = 16.9 for T = 298 K.

For the redox system in section 5 we have: I–1 = 22–1 = 21 (K^{+1} is omitted again), G=5 ($\mathbf{x}$ = (E, pH, pSO_4, pMn2, pFe2)^T, the number equilibrium constants: 16; then 5+16 = 21. For the non-redox system in section 4 we have: I–1 = 36–1 = 35 (Na^{+1} is omitted), G=7 (x = (pH, pSO_4, pNH_3, pZn, $pC_{20}H_{10}N_3O_7S$, $pC_{10}H_{12}N_2O_8$, pCl)^T, where: $pC_{20}H_{10}N_3O_7S$ = –log[$C_{20}H_{10}N_3O_7S^{-3}$], $pC_{10}H_{12}N_2O_8$ = –log[$C_{10}H_{12}N_2O_8^{-4}$], pCl = -log[Cl^{-1}], and the number of equilibrium constants involved in relations for the equilibrium constants is 27; then 35 = (7+27) + 1.

VII. ON TWO ALTERNATIVE METHODS OF SEARCHING THE DEPENDENCY OR IN-DEPENDENCY

The linear dependency or independency of balances for non-redox or redox systems were considered above from the viewpoint of 0 = 0 identity criterion, promoted in this work. In matrix algebra, this problem is resolvable with use of the Kronecker–Capelli theorem and the Gaussian elimination method [17-20].

The set of G balances in Eq. 9 can be presented in a matrix form as follows

$$\mathbf{AN} = \mathbf{BN_0} \tag{39}$$

where:

$$(a)\ \mathbf{A} = \mathbf{A}_{G \times I} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1I} \\ a_{21} & a_{22} & \cdots & a_{2I} \\ \vdots & \vdots & \ddots & \vdots \\ a_{G1} & a_{G2} & \cdots & a_{GI} \end{bmatrix} ;\ (b)\ \mathbf{N} = \begin{bmatrix} N_1 \\ N_2 \\ \vdots \\ N_I \end{bmatrix} ;\ (c)\ \mathbf{B} = \begin{bmatrix} b_{11} & \cdots & b_{1J} \\ b_{21} & \cdots & b_{2J} \\ \vdots & \ddots & \vdots \\ b_{G1} & & b_{GJ} \end{bmatrix} ;\ (d)\ \mathbf{N}_0 = \begin{bmatrix} N_{01} \\ N_{02} \\ \vdots \\ N_{0J} \end{bmatrix} \tag{40}$$

For computational needs, the augmented matrix of **A|B** type is considered

$$\mathbf{A|B} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1I} & b_{11} & \cdots & b_{1J} \\ a_{21} & a_{22} & \cdots & a_{2I} & b_{21} & \cdots & b_{2J} \\ \vdots & \vdots & \cdots & \vdots & \vdots & \ddots & \vdots \\ a_{G1} & a_{G2} & \cdots & a_{GI} & b_{G1} & & b_{GJ} \end{bmatrix} \tag{41}$$

The principal idea of the Gaussian elimination method, perceived as row reduction of a matrix **A** (Eq. 40a), is characterized by step- by- step elimination of the variables. It is based on an addition of one equation to the linear combination of the others in order to eliminate a first variable, and to continue this procedure until only one variable is left. Once this final variable is determined, its value is substituted back into the other equations in order to evaluate the remaining unknowns. The operations made on rows and columns of a coefficient matrix **A** do not change its rank, r, are called as *elementary operations*. As a result of these operations, the matrix **A** is transformed into an upper triangular matrix, named also as a matrix in reduced row echelon form. Generally, it is an extremely extensive procedure, even in the very simple cases, shown e.g. in [21,22].

The Kronecker-Capelli theorem states that the system of equations has a solution if and only if the rank of the main matrix **A** is equal to the rank r of the augmented matrix, i.e., r = *rank*(**A**) = *rank*(**A|B**).

The Gaussian elimination and the Kronecker-Capelli theorem are usually referred to (illustrated by) 'small' matrices $\mathbf{A}_{G \times I}$ (Eq. 40a), similar in its shape to the square matrices.

If we choose any h rows and h columns of the matrix $\mathbf{A} = \mathbf{A}_{G \times I}$, then the elements at the intersections of these rows and columns form a square h×h matrix; the determinant $M_{h \times h}$ is one of the minors of this matrix. Then after deleting G–h rows and I–h columns from the matrix $\mathbf{A}_{G \times I}$, where h ≤ *min*(G,I), we obtain $\binom{G}{h}\binom{I}{h}$ minors $M_{h \times h}$,

where

$$\binom{n}{h} = \frac{n!}{h!\,(n-h)!} \qquad (n = G, I) \tag{42}$$

is the binomial coefficient. For example, a square matrix $\mathbf{A}_{5 \times 5}$ contains $\binom{5}{0}\binom{5}{0} = 1$ minor of the order 5–0 = 5;

$\binom{5}{1}\binom{5}{1} = 25$ minors of the order 5–1 = 4, $\binom{5}{2}\binom{5}{2} = 100$ minors of the order 5–2 = 3; and $\binom{5}{3}\binom{5}{3} = 100$ minors

of the order 5–3 = 2. From the above it is clear that finding the rank (r = *rank*(**A**)) of such a matrix by direct calculation of all its minors would be a very laborious task, not recommended in practice, especially when compared with the (advised) transformation of linear combination to identity, 0 = 0.

Summarizing, both alternative methods, although simple from arithmetic viewpoint, are time-consuming/tedious, and therefore easily susceptible to mistakes – especially in the cases where the dimensions of the matrix $\mathbf{A}_{G \times I}$ are large. Application of the matrix notation for checking the linear dependency or independency appears to be uncomfortable/awkward in notation, especially when the number I of kinds of the species is significant, not falling within a single line. The advantage (superiority) of the identity (0 = 0) method over the Gaussian elimination method and application of the Kronecker–Capelli theorem is indisputable, especially in relation to complex electrolytic systems.

VIII.   FINAL COMMENTS

The problem of linear dependency or independency of equations is of fundamental importance in GATES/GEB [10]. The rank of the related matrix is a natural consequence of this problem. The matrix's rank appears to be one of its most fundamental characteristics in formulation of electrolytic systems, perceived as a hidden connection of physicochemical laws of the matter conservation. Among others, it provides a criterion distinguishing between redox and non-redox electrolytic systems. An independent equation obtained from charge and elemental and/or core balances related to electrolytic redox systems provides the independent equation known as Generalized Electron Balance (GEB).

A simple, recommended manner of reducing the set of equations for a non-redox system to identity 0 = 0, is based on 'painting' the related, mutually reducing components of the linear combination of the equations, prepared according to the pre-assumed mode. On this basis, one can draw the following, very important conclusions specified in section 6, that can be generalized on systems with different degrees of complexity.

It should necessarily be stressed that the balances for an electrolytic system impose certain (not any-one) coefficients in **A** and **B** (Eqs. 40a,c). What's more, we will see that the multipliers/factors of the appropriate (purposeful) equations forming the linear combination of the starting elemental equations, have a specific interpretation, associated with oxidation numbers (ω_g) of the corresponding elements. This is another, important remark unknown in earlier literature. Thus the conditions of the chemical (elemental balances) and physical (charge balance, ChB) nature simplify decidedly the issue, when compared with the Gauss elimination method and Kronecker-Capelli theorem. From this it follows that the determination of the rank of the matrix, and thus determination of the number of independent equations according to the identity (0 = 0) method is incomparably simpler and less time-consuming than checking the rank of the matrix with the coefficients whose values are not subjected to any, preliminary assumptions.

All the regularities stated (here and elsewhere) on the basis of mathematical analysis of the systems of different complexity, enable to put forward a thesis that the dependency/independency property is of general nature, applicable to non-redox and redox electrolytic systems, of any degree of complexity. A keystone for the overall, thermodynamic knowledge on electrolytic systems is the linear combination $2 \cdot f(\text{O}) - f(\text{H})$ of elemental balances: $f(\text{H})$ for H and $f(\text{O})$ for O. The $2 \cdot f(\text{O}) - f(\text{H})$ 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 equation for $2 \cdot f(\text{O}) - f(\text{H})$, considered as the *pr*imary form of GEB and denoted as *pr*-GEB

$$\therefore \quad pr - \text{GEB} \quad = 2 \cdot f(\text{O}) \ - \ f(\text{H})$$

is the basis of GEB formulation according to Approach II to GEB [1-9,11,12,23-34]. The $2 \cdot f(\text{O}) - f(\text{H})$ is linearly independent on ChB and other balances, for elements/cores $f(\text{Y}_m) \neq$ H, O, in any redox system. For any non-redox system, $2 \cdot f(\text{O}) - f(\text{H})$ is linearly dependent on those balances [2,4,12,23]. Then the linear independency/dependency of $2 \cdot f(\text{O}) - f(\text{H})$ on the other balances is the general criterion distinguishing between redox and non-redox systems. Hence, it is clear that the elemental balances: $f(\text{H})$ and $f(\text{O})$ are not involved in mathematical description of non-redox systems. This statement can be generalized to non-redox systems of any degree of complexity [4,12].

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