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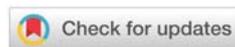[2]Department of Analytical Chemistry, Cracow University of Technology, 31-155 Cracow, Poland

Research Article

Further remarks on the new criterion differentiating between Non–Redox and Redox Electrolytic Systems

Abstract

The new general criterion, distinguishing between non-redox and redox electrolytic systems, is based on the properties of the linear combination $f_{12} = 2 \cdot f(O) - f(H)$ of elemental balances: $f_1 = f(H)$ for $Y_1 =$ H, and $f_2 = f(O)$ for $Y_2 = O$. The f_{12} is the *pr*imary form of the Generalized Electron Balance ($f_{12} = pr$GEB), completing the set of balances needed to formulate a redox system, according to Generalized Approach to Electrolytic Systems (GATES). In the redox system, f_{12} is linearly independent on charge ($f_0 = ChB$) and other elemental/core balances $f_k = f(Y_k)$ (k=3,...,K), i.e., $f_0, f_{12}, f_3,...,f_K$ form the set of independent balances needed to formulate the redox system. In a non-redox system, f_{12} is linearly dependent on the balances $f_0, f_3,...,f_K$, i.e., $f_0, f_3,...,f_K$ form the set of K − 1 independent balances needed to formulation of the non-redox system. Further properties, resulting from the combination of these equations specified here, are involved with oxidation numbers (ONs) of elements in components forming a non-redox or redox system. In the GEB formulation, made according to Approach II to GEB, the prior knowledge of oxidation numbers for all elements of the system is not needed. Moreover, 'oxidant' and 'reductant' are derivative/redundant terms. The mathematical knowledge, required to answer the question put in the title, is comprised within the four basic, algebraic operations. These properties are illustrated on a complex (41 species) example of a dynamic D+T redox system, and its static non-redox (T, D) subsystems.

Introduction

Electrolytic systems, of different degree of complexity, can be resolved according to Generalized Approach to Electrolytic Systems (GATES) [1–3], principles, perceived as the best thermodynamic approach to equilibrium and metastable [4–6] systems, where all attainable physicochemical knowledge on a system tested can be involved. The advantages of GATES are particularly related to redox systems, where the Generalized Electron Balance (GEB) is formulated within GATES/GEB ⊂ GATES [1–3,6–34].

All the inferences made within GATES/GEB are based on firm, algebraic foundations. It allows to understand far better all physicochemical phenomena occurring in a system in question, and improve some methods of analysis. All the facts confirm the huge potency of simulated calculations made according to GATES/GEB principles, with all attainable and preselected physicochemical knowledge involved therein.

This paper provides an example of a dynamic electrolytic redox system realized according to titrimetric mode, where V mL of titrant T is added, up to a given point of the titration, into V_o mL of titrand D, and V_o+V mL of D+T mixture is thus obtained, if the additivity of the volumes is pre–assumed/valid. For modelling purposes, the titration is considered as the isothermal process realized in the closed system, separated from the environment by diathermal walls. The related system will be formulated according to the GATES principles, and resolved with use of iterative computer program MATLAB [35,36]. The problem of oxidation numbers (ONs) calculation on the step of formulation of D+T mixture and its subsystems (D, T) is also considered.

The GATES and GATES/GEB principles were also extended on multi–solvent media, with amphiprotic (co)solvent(s) involved [37–40].

Preliminary notations

According to GATES/GEB principles, any species $X_i^{z_i}$ in an electrolytic system can be perceived in its natural form, i.e., as a hydrate $X_i^{z_i} - n_{iW}$ in aqueous (W=H_2O) solution, where z_i ($z_i = 0, \pm1, \pm2,...$) is the external charge of $X_i^{z_i}$, expressed in terms of elementary charge unit e = F/N_A (F – Faraday constant, N_A – Avogadro's number), and $n_i \equiv n_{iW} \equiv n_i H_2O$ (≥ 0) is the mean number of water (W = H_2O) molecules attached to $X_i^{z_i}$. The known chemical formulas of $X_i^{z_i}$ (i = 1,...,I)

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provide the information necessary/sufficient to formulate the respective balances.

As were stated above, the terms: components and species are distinguished, for the balancing purposes. In the notation applied here, N_{oj} (j=1,2,...,J) be the number of molecules of a component of j-th kind, composing a static (D, T) or dynamic D+T system, whereby the D and T are composed separately, from defined components, including water. 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), where $n_i \equiv n_{iW} \equiv n_i H_2O$; then we have: H^{+1} (N_2,n_2), OH^{-1} (N_3,n_3),..., for ordering purposes. Molar concentration of the species $X_i^{Z_i} \cdot n_{iW}$ in D+T system is denoted as $[X_i^{Z_i}]$.

The GEB is recognized as the law of Nature [1,41], as the hidden connection of physicochemical laws, and as the breakthrough in thermodynamic theory of electrolytic redox systems. The GEB was discovered by Michałowski: as the Approach I to GEB (1992), and as the Approach II to GEB (2005). In the Approach I to GEB, perceived according to 'card game' principle, electron-active elements are perceived as 'players', electron-non-active elements as 'fans', and electrons as 'money'; the knowledge of oxidation numbers is needed here. The Approach II introduces the balance $f_{12} = 2 \cdot f_2 - f_1$ as the combination of elemental balances: $f_1 = f(H)$ for $Y_1 = H$ and $f_2 = f(O)$ for $Y_2 = O$. Charge balance ($f_0 = ChB$) and other, elemental and/or core balances $f_k = f(Y_k)$ ($Y_k \neq H$, O; k=3,...,K) are also considered within GATES. A core is a cluster of different atoms with defined composition (expressed by chemical formula), structure and external charge, unchanged in the system considered. In a redox system, f_{12} is linearly independent on the balances $f_0, f_3,...,f_K$, i.e., a redox system is formulated with use of K independent balances $f_0, f_{12}, f_3,...,f_K$ that form the complete set of algebraic equations needed for the solution of the redox system, according to GATES/GEB principles.

In a non-redox system, the f_{12} is linearly dependent on the balances: $f_0, f_3, ...,f_K$, i.e., a non–redox system is formulated with use of K−1 independent balances $f_0, f_3,...,f_K$. The balances f_1 and f_2, and then f_{12}, are not used for the solution of a non–redox system. The linear dependency or independency of f_{12} from $f_0, f_3,...,f_K$ is then the general property distinguishing between non-redox and redox systems, of any degree of complexity [40,41].

Other, general properties are also valid here, within GATES. Among others, oxidation number (ON) is the derivative concept, resulting from linear combination of the balances. Application of controversial electronegativity (EN) concept, where a highly doubtful (artificial) qualification of ionic bonds (practiced hitherto in literature) is made, is thus avoided. There is no need to pre-assign the roles of oxidants and reducers to individual components and species; oxidant and reductant are derivative concepts within GATES/GEB.

Formulation of GEB according to Approach II needs none prior knowledge of ONs of elements in all components forming a system and in all species present in the system. For a redox

system with K−K^* 'players', f_{12} is linearly independent on f_0, $f_3,..., f_K$, i.e., the redox system is described by K independent balances f_0, f_{12}, $f_3,..., f_K$. For a non-redox system (K^*=K), f_{12} is linearly dependent on f_0, $f_3,..., f_K$, i.e., a non-redox system is described by K−1 independent balances $f_0, f_3,...,f_K$. Consequently, the linear combination $f_{12} + f_0 - \Sigma_{k=3}^{K^*} d_k \cdot f_k$ $\Leftrightarrow \Sigma_{k=3}^{K^*} d_k \cdot f_k - f_0$ with d_k equal to the oxidation numbers of the related elements, is reducible to identity, $0 = 0$. The linear combination $\Sigma_{k=1}^{K^*} d_k \cdot f_k - f_0$ applied to a redox system does not give the identity, also after further combination with K − K^* balances for 'players'. The linear combination $\Sigma_{k=1}^{K^*} d_k \cdot f_k - f_0$ for a redox system is composed only of components and species, where 'players' are involved. These regularities are confirmed also in the examples presented below. On this basis, we express/confirm our conviction that these regularities are valid for electrolytic systems of any degree of complexity, with biological systems included *a priori*.

The charged/ionic species $X_i^{Z_i} \cdot n_{iW}$, i.e., the species with $z_i \neq 0$ ($z_i > 0$ for cations, $z_i < 0$ for anions), are involved in charge balance, $f_0 = ChB$,

$$f_0 = \Sigma_{i=2}^{I} z_i \cdot N_i = 0 \Rightarrow \Sigma_{i=2}^{I} z_i \cdot \left[X_i^{Z_i} \right] = 0 \qquad (1)$$

The terms: charge balance will be used to both forms of this relation, in accordance with the Ockham razor principle; this should not lead to ambiguity, in the right context. The same viewpoint is referenced to generalized electron balance (GEB). The elemental/core balances, when expressed in terms of molar concentrations, are named as concentration balances.

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

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

$$f_2 = f(O) = 2N_1 + \Sigma_{i=2}^{I} (a_{2i} + 2n_{iw}) \cdot N_i - \Sigma_{j=1}^{J} b_{2j} \cdot N_{oj} = 0 \qquad (3)$$

Then the balance

$$f_{12} = 2 \cdot f_2 - f_1 = \Sigma_{i=2}^{I} (2 \cdot a_{2i} - a_{1i}) \cdot N_i - \Sigma_{j=1}^{J} (2 \cdot b_{2j} - b_{1j}) \cdot N_{oj} = 0 \qquad (4)$$

is formulated.

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

$$f_k = f(Y_k) = \sum_{i=1}^{I} a_{ki} \cdot N_i - \sum_{j=1}^{J} b_{kj} \cdot N_{oj} = 0 \quad (k=3,...,K) \qquad (5)$$

where a_{ki} and b_{kj} are the numbers of elements/cores Y_k in $X_i^{Z_i} \cdot n_{iW}$, and in the j-th component of the system,, resp. For example, N_5 species/ions $HSO_4^{-1} \cdot n_5 H_2O$ involve $N_5(1+2n_5)$ atoms of H (where a_{12}=1), $N_5(4+n_5)$ atoms of O (where a_{22}=4),

and N_5 atoms of S; N_{04} molecules of $FeSO_4 \cdot 7H_2O$ as a component involve $14N_{04}$ atoms of H, $11N_{04}$ atoms of O, N_{04} atoms of S and N_{04} atoms of Fe.

Formulation of linear combinations is applicable to check the linear dependency or independency of the balances f_0, f_{12}, f_3,...,f_K. For this purpose we will try, in all instances, to obtain the simplest form of the linear combination of these balances. A very useful/effective manner for checking/stating the linear dependence of f_0, f_{12}, f_3, ...,f_K related to a non-redox system, is the transformation of their linear combination to the identity, 0 = 0. For a redox system, the proper linear combination of the balances gives the simplest/shortest form of GEB.

To avoid possible/simple mistakes made in the realization of the linear combination procedure, we *apply the equivalent relations:*

$$f_k = \sum_{i=1}^{I} a_{ki} \cdot N_i - \sum_{j=1}^{J} b_{kj} \cdot N_{oj} = 0 \Leftrightarrow \sum_{i=1}^{I} a_{ki} \cdot N_i = \sum_{j=1}^{J} b_{kj} \cdot N_{oj} = 0$$
(6a)

for elements with negative oxidation numbers, or

$$-f_k = \sum_{i=1}^{I} b_{kj} \cdot N_{oj} = \sum_{i=1}^{I} a_{ki} \cdot N_{oi} = 0 \Leftrightarrow \sum_{j=1}^{J} b_{kj} \cdot N_{oj} = \sum_{i=1}^{J} b_{ki} \cdot N_i$$
(6b)

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

The linear combination

$$f_0 + f_{12} - \sum_{k}^{k} d_k \cdot f_k = 0 \Leftrightarrow \sum_{k}^{k} d_k \cdot f_k - f_{12} - f_0 = 0 \Leftrightarrow$$

$$f_1 - 2f_2 + \sum_{k=3}^{k} d_k \cdot f_k - f_0 = 0 \Leftrightarrow \sum_{k=1}^{k} d_k \cdot f_k - f_0 = 0$$
(7)

involves K balances: f_0, f_{12}, f_3,...,f_K. In particular, $d_1 = +1$, $d_2 = -2$. As will be indicated below, the multipliers d_k are equal to (or involved with) the oxidation numbers (ON's) of the corresponding elements E_k, $Y_k = E_k$ ($k \in 1,...,K$). It enables to get the simplest (most desired) form of the related linear combination (Equation 7), as will be explained in examples presented below.

In Equation 4 and then in Equation 7, the terms involved with water, i.e., N_1, N_{oj} (for j related to H_2O as the component, also as hydrating water), and $n_i = n_{iW}$ are not involved. The necessity of prior knowledge of n_{iW} values in the balancing is thus avoided, already at the stage of f_{12} formulation.

Consequently, the set of K independent balances: f_0, f_{12}, f_3,... ,f_K is related to a redox system, whereas f_0, f_3, ...,f_K form the set of K−1 independent balances related to a non-redox system, where f_3,...,f_K is the set of K−2 elemental/core balances $f_k = f(Y_k)$ for k=3,...,K, i.e., for $Y_k \neq$ H, O (Equation 5). The balancing is necessary for computer simulation of titrimetric procedure according to GATES principles.

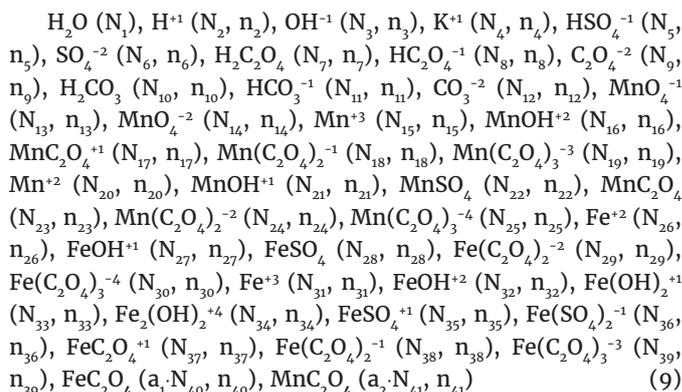The elemental/core balances, expressed in terms of

particular units: N_{oj} for components and N_i for species, are the basis to formulation of Generalized Electron Balance (GEB), charge balance (ChB) and concentration balances, expressed in terms of molar concentrations, see Equation 1.

Formulation of electrolytic D+T system

Preliminary information: As an example let us consider the dynamic D+T system, where V_o mL of titrand (D) containing $FeSO_4$ (C_{01} mol/L), $H_2C_2O_4$ (C_{02} mol/L), (H_2SO_4, C_{03} mol/L) and CO_2 (C_{04} mol/L) is titrated with V mL $KMnO_4$ (C mol/L) and CO_2 (C_1 mol/L) as titrant (T). The CO_2 (C_{04}, C_1) in D and T is considered as an admixture, resulting from a contact with air, before the titration. The CO_2 (as H_2CO_3, HCO_3^{-1} and CO_3^{-2}) is the product of $H_2C_2O_4$ oxidation represented, stoichiometrically, by the reaction

$$2MnO_4^{-1} + 5H_2C_2O_4 + 6H^{+1} = 2Mn^{+2} + 10CO_2 + 8H_2O \tag{8}$$

It is assumed that the D+T system is composed of $KMnO_4$ (N_{01} molecules) + CO_2 (N_{02}) + H_2O (N_{03}) in V mL of T and $FeSO_4 \cdot 7H_2O$ (N_{04}) + $H_2C_2O_4 \cdot 2H_2O$ (N_{05}) + H_2SO_4 (N_{06}) + CO_2 (N_{07}) + H_2O (N_{08}) in V_o mL of D. 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 ($a_1 \cdot N_{40}$, n_{40}), MnC_2O_4 ($a_2 \cdot N_{41}$, n_{41}) $\tag{9}$

The molecules of the (pre-assumed) precipitates of the oxalates are written in bold: **FeC_2O_4** and **MnC_2O_4**; $a_i = 1$, if the precipitate indicated (i = 1, 2) is the equilibrium solid phase in the system; otherwise, $a_i = 0$.

Formulation of balances for D+T system according to approach I

The charge and elemental/core balances, formulated on the basis of the data specified above for electron-non-active elements ('fans') are as follows:

$f_0 = ChB$

$N_2 - N_3 + N_4 - N_5 - 2N_6 - N_8 - 2N_9 - N_{11} - 2N_{12} - N_{13} - 2N_{14} + 3N_{15} + 2N_{16} +$

$N_{17} - N_{18} - 3N_{19} + 2N_{20} + N_{21} - 2N_{24} - 4N_{25} + 2N_{26} + N_{27} - 2N_{29} - 4N_{30} + 3N_{31} +$

$2N_{32} + N_{33} + 4N_{34} + N_{35} - N_{36} + N_{37} - N_{38} - 3N_{39} = 0$
(10)

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + 2N_4n_4 + N_5(1+2n_5) + 2N_6n_6 + N_7(2+2n_7) + N_8(1+2n_8) + 2N_9n_9 +$

$N_{10}(2+2n_{10}) + N_{11}(1+2n_{11}) + 2N_{12}n_{12} + 2N_{13}n_{13} + 2N_{14}n_{14} + 2N_{15}n_{15} + N_{16}(1+2n_{16}) + 2N_{17}n_{17} +$

$2N_{18}n_{18} + 2N_{19}n_{19} + 2N_{20}n_{20} + N_{21}(1+2n_{21}) + 2N_{22}n_{22} + 2N_{23}n_{23} + 2N_{24}n_{24} + 2N_{25}n_{25} + 2N_{26}n_{26} +$

$N_{27}(1+2n_{27}) + 2N_{28}n_{28} + 2N_{29}n_{29} + 2N_{30}n_{30} + 2N_{31}n_{31} + N_{32}(1+2n_{32}) + N_{33}(2+2n_{33}) + N_{34}(2+2n_{34}) +$

$2N_{35}n_{35} + 2N_{36}n_{36} + 2N_{37}n_{37} + 2N_{38}n_{38} + 2N_{39}n_{39} + 2a_1 \cdot N_{40}n_{40} + 2a_2 \cdot N_{41}n_{41}$

$= 2N_{03} + 14N_{04} + 6N_{05} + 2N_{06} + 2N_{08}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4n_4 + N_5(4+n_5) + N_6(4+n_6) + N_7(4+n_7) + N_8(4+n_8) + N_9(4+n_9) +$

$N_{10}(3+n_{10}) + N_{11}(3+n_{11}) + N_{12}(3+n_{12}) + N_{13}(4+n_{13}) + N_{14}(4+n_{14}) + N_{15}n_{15} + N_{16}(1+n_{16}) + N_{17}(4+n_{17}) +$

$N_{18}(8+n_{18}) + N_{19}(12+n_{19}) + N_{20}n_{20} + N_{21}(1+n_{21}) + N_{22}(4+n_{22}) + N_{23}(4+n_{23}) + N_{24}(8+n_{24}) + N_{25}(12+n_{25}) +$

$N_{26}n_{26} + N_{27}(1+n_{27}) + N_{28}(4+n_{28}) + N_{29}(8+n_{29}) + N_{30}(12+n_{30}) + N_{31}n_{31} + N_{32}(1+n_{32}) + N_{33}(2+n_{33}) +$

$N_{34}(2+n_{34}) + N_{35}(4+n_{35}) + N_{36}(8+n_{36}) + N_{37}(4+n_{37}) + N_{38}(8+n_{38}) + N_{39}(12+n_{39}) + a_1 \cdot N_{40}(4+n_{40}) +$

$a_2 \cdot N_{41}(4+n_{41}) = 4N_{01} + 2N_{02} + N_{03} + 11N_{04} + 6N_{05} + 4N_{06} + 2N_{07} + N_{08}$

$-f_3 = -f(K)$

$N_{01} = N_4$ (11)

$-6f_4 = -f(S) = -6f(SO_4)$

$6(N_{04} + N_{06}) = 6(N_5 + N_6 + N_{22} + N_{28} + N_{35} + 2N_{36})$ (12)

$f_5 = f(C)$

$2(N_7 + N_8 + N_9) + (N_{10} + N_{11} + N_{12}) + 2N_{17} + 4N_{18} + 6N_{19} + 2N_{23} + 4N_{24} + 6N_{25} + 4N_{29} + 6N_{30} +$

$2N_{37} + 4N_{38} + 6N_{39} + 2a_1 \cdot N_{40} + 2a_2 \cdot N_{41} = N_{02} + 2N_{05} + N_{07}$ (13)

$f_6 = f(Fe)$

$N_{26} + N_{27} + N_{28} + N_{29} + N_{30} + N_{31} + N_{32} + N_{33} + 2N_{34} + N_{35} + N_{36} + N_{37} + N_{38} + N_{39} + a_1 \cdot N_{40} = N_{04}$ (14)

$f_7 = f(Mn)$

$N_{13} + N_{14} + N_{15} + N_{16} + N_{17} + N_{18} + N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + a_2 \cdot N_{41} = N_{01}$ (15)

Linear combinations of the balances

On the basis of charge and elemental/core balances, we formulate the linear combinations:

$f_{12} = 2 \cdot f_2 - f_1$ (16)

$-N_2 + N_3 + 7N_5 + 8N_6 + 6N_7 + 7N_8 + 8N_9 + 4N_{10} + 5N_{11} + 6N_{12} + 8N_{13} + 8N_{14} + N_{16} +$

$8N_{17} + 16N_{18} + 24N_{19} + N_{21} + 8N_{22} + 8N_{23} + 16N_{24} + 24N_{25} + N_{27} + 8N_{28} + 16N_{29} + 24N_{30} +$

$N_{32} + 2N_{33} + 2N_{34} + 8N_{35} + 16N_{36} + 8N_{37} + 16N_{38} + 24N_{39} + a_1 \cdot 8N_{40} + a_1 \cdot 8N_{41}$

$= 8N_{01} + 4N_{02} + 8N_{04} + 6N_{05} + 6N_{06} + 4N_{07}$ (16a)

$f_{12} + f_0 - f_3 - 6f_4$ (17)

$6(N_7 + N_8 + N_9) + 4(N_{10} + N_{11} + N_{12}) + 7N_{13} + 6N_{14} + 3(N_{15} + N_{16}) + 9N_{17} + 15N_{18} + 21N_{19} +$

$2(N_{20} + N_{21} + N_{22}) + 8N_{23} + 14N_{24} + 20N_{25} + 2(N_{26} + N_{27} + N_{28}) + 14N_{29} + 20N_{30} +$

$3(N_{31} + N_{32} + N_{33} + 2N_{34} + N_{35} + N_{36}) + 9N_{37} + 15N_{38} + 21N_{39} + a_1 \cdot 8N_{40} + a_2 \cdot 8N_{41} =$

$7N_{01} + 4(N_{02} + N_{07}) + 2N_{04} + 6N_{05}$ (17a)

Applying atomic numbers: $Z_C = 6$ for C, $Z_{Fe} = 26$ for Fe and $Z_{Mn} = 25$ for Mn, from Equations (13) – (15) and (17a) we have, by turns:

$Z_C \cdot f_5 = Z_C \cdot f(C)$

$Z_C \cdot (2(N_7 + N_8 + N_9) + (N_{10} + N_{11} + N_{12}) + 2N_{17} + 4N_{18} + 6N_{19} + 2N_{23} + 4N_{24} + 6N_{25} + 4N_{29} + 6N_{30} +$

$2N_{37} + 4N_{38} + 6N_{39} + 2a_1 \cdot N_{40} + 2a_2 \cdot N_{41}) = Z_C \cdot (N_{02} + 2N_{05} + N_{07})$ (13a)

$Z_{Fe} \cdot f_6 = Z_{Fe} \cdot f(Fe)$

$Z_{Fe} \cdot (N_{26} + N_{27} + N_{28} + N_{29} + N_{30} + N_{31} + N_{32} + N_{33} + 2N_{34} + N_{35} + N_{36} + N_{37} + N_{38} + N_{39} + a_1 \cdot N_{40})$

$= Z_{Fe} \cdot N_{04}$ (14a)

$Z_{Mn} \cdot f_7 = Z_{Mn} \cdot f(Mn)$

$Z_{Mn} \cdot (N_{13} + N_{14} + N_{15} + N_{16} + N_{17} + N_{18} + N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + a_2 \cdot N_{41})$

$= Z_{Mn} \cdot N_{01}$ (15a)

$Z_C \cdot f_5 + Z_{Fe} \cdot f_6 + Z_{Mn} \cdot f_7 - (f_{12} + f_0 - f_3 - 6f_4)$ (18)

$Z_C \cdot (2(N_7 + N_8 + N_9) + (N_{10} + N_{11} + N_{12}) + 2(N_{17} + 2N_{18} + 3N_{19}) + 2(N_{23} + 2N_{24} + 3N_{25}) +$

$2(2N_{29} + 3N_{30}) + 2(N_{37} + 2N_{38} + 3N_{39}) + 2a_1 \cdot N_{40} + 2a_2 \cdot N_{41}) + Z_{Fe} \cdot (N_{26} + N_{27} + N_{28} + N_{29} +$

$N_{30} + N_{31} + N_{32} + N_{33} + 2N_{34} + N_{35} + N_{36} + N_{37} + N_{38} + N_{39} + a_1 \cdot N_{40}) + Z_{Mn} \cdot (N_{13} + N_{14} + N_{15} +$

$N_{16} + N_{17} + N_{18} + N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + a_2 \cdot N_{41}) - (6(N_7 + N_8 + N_9) +$

$4(N_{10} + N_{11} + N_{12}) + 7N_{13} + 6N_{14} + 3(N_{15} + N_{16}) + 9N_{17} + 15N_{18} + 21N_{19} + 2(N_{20} + N_{21} + N_{22}) +$

$8N_{23} + 14N_{24} + 20N_{25} + 2(N_{26}+N_{27}+N_{28}) + 14N_{29} + 20N_{30} + 3(N_{31} + N_{32} + N_{33} + 2N_{34} + N_{35} + N_{36}) +$

$9N_{37} + 15N_{38} + 21N_{39} + a_1 \cdot 8N_{40} + a_2 \cdot 8N_{41})$

$= Z_C \cdot (N_{02}+2N_{05}+N_{07}) + Z_{Fe} \cdot N_{04} + Z_{Mn} \cdot N_{01} - (7N_{01} + 4(N_{02} + N_{07}) + 2N_{04} + 6N_{05}) \quad \Rightarrow$

$2(Z_C - 3)(N_7 + N_8 + N_9) + (Z_C - 4)(N_{10} + N_{11} + N_{12}) + (Z_{Fe} - 2)(N_{26} + N_{27} + N_{28}) +$

$(Z_{Fe} - 3)(N_{31} + N_{32} + N_{33} + 2N_{34} + N_{35} + N_{36}) + (Z_{Mn} - 7)N_{13} + (Z_{Mn} - 6)N_{14} +$

$(Z_{Mn} - 3)(N_{15} + N_{16}) + (Z_{Mn} - 2)(N_{20} + N_{21} + N_{22}) + a_1 \cdot (Z_{Fe} + 1 \cdot 2 \cdot Z_C - 8)N_{40} +$

$(Z_{Fe}+2 \cdot 2 \cdot Z_C - 14)N_{29} + (Z_{Fe} + 3 \cdot 2 \cdot Z_C - 20)N_{30} + (Z_{Fe} + 1 \cdot 2 \cdot Z_C - 9)N_{37} +$

$(Z_{Fe} + 2 \cdot 2 \cdot Z_C - 15)N_{38} + (Z_{Fe} + 3 \cdot 2 \cdot Z_C - 21)N_{39} + (Z_{Mn} + 1 \cdot 2 \cdot Z_C - 8) \cdot (N_{23} + a_2 \cdot N_{41}) +$

$(Z_{Mn} + 2 \cdot 2 \cdot Z_C - 14) \cdot N_{24} + (Z_{Mn} + 3 \cdot 2 \cdot Z_C - 20)N_{25} + (Z_{Mn} + 1 \cdot 2 \cdot Z_C - 9)N_{17} +$

$(Z_{Mn} + 2 \cdot 2 \cdot Z_C - 15)N_{18} + (Z_{Mn} + 3 \cdot 2 \cdot Z_C - 21)N_{19}$

$= 2(Z_C - 3)N_{05} + (Z_C - 4)(N_{02} + N_{07}) + (Z_{Fe} - 2)N_{04} + (Z_{Mn} - 7)N_{01}$
$\hfill (19)$

Equation 19 will be compared with the one obtained according to Approach I to GEB, introduced initially (as such) in the papers [42–47] and applied for modelling of titrations curves, realized according to modified Gran I and II methods, in numerous versions [48–52], proposed by Michałowski.

Equivalency of Approaches I and II to GEB

The Approach I to GEB needs prior knowledge of ONs for the 'players', i.e., C, Fe and Mn, in different components and species formed by them, in the D+T system considered. It is assumed there, that both 'players' as components introduce, to the common pool, a certain number of their own electrons, namely:

In V mL of T, N_{01} molecules of $KMnO_4$ introduce $(Z_{Mn}-7)N_{01}$ manganese electrons, N_{02} molecules of CO_2 introduce $(Z_C - 4)N_{02}$ carbon electrons;

In V_0 mL of D, N_{04} molecules of $FeSO_4 \cdot 7H_2O$ introduce $(Z_{Fe}-2)N_{04}$ iron electrons, N_{05} molecules of $H_2C_2O_4 \cdot 2H_2O$ introduce $2(Z_C-3)N_{05}$ carbon electrons, and N_{07} molecules of CO_2 introduce $(Z_C - 4)N_{07}$ carbon electrons.

Then the total number of electrons introduced by the 'players' is

$(Z_{Mn} - 7)N_{01} + 2(Z_C - 3)N_{01} + (Z_C - 4)(N_{02} + N_{07}) + (Z_{Fe} - 2)N_{04}$

These electrons are 'dissipated' between different species

formed in the system by C, Fe and Mn. In effect:

N_7 molecules of $H_2C_2O_4 \cdot n_7H_2O$ carries $2(Z_C - 3)N_7$ carbon electrons;

N_8 ions of $HC_2O_4^{-1} \cdot n_8H_2O$ carries $2(Z_C - 3)N_8$ carbon electrons;

N_9 ions of $C_2O_4^{-2} \cdot n_9H_2O$ carries $2(Z_C - 3)N_9$ carbon electrons;

N_{10} molecules of $H_2CO_3 \cdot n_{10}H_2O$ carries $(Z_C - 4)N_{10}$ carbon electrons;

N_{11} ions of $HCO_3^{-1} \cdot n_{11}H_2O$ carries $(Z_C - 4)N_{11}$ carbon electrons;

N_{12} ions of $CO_3^{-2} \cdot n_{12}H_2O$ carries $(Z_C - 4)N_{12}$ carbon electrons;

N_{13} ions of $MnO_4^{-1} \cdot n_{13}H_2O$ carries $(Z_{Mn} - 7)N_{13}$ manganese electrons;

N_{14} ions of $MnO_4^{-2} \cdot n_{14}H_2O$ carries $(Z_{Mn} - 6)N_{14}$ manganese electrons;

N_{15} ions of $Mn^{+3} \cdot n_{15}H_2O$ carries $(Z_{Mn} - 3)N_{15}$ manganese electrons;

N_{16} ions of $MnOH^{+2} \cdot n_{16}H_2O$ carries $(Z_{Mn} - 3)N_{16}$ manganese electrons;

N_{17} ions of $MnC_2O_4^{+1} \cdot n_{17}H_2O$ carries $(Z_{Mn} - 3)N_{17}$ manganese electrons and $2(Z_C - 3)N_{17}$ carbon electrons; together $(Z_{Mn}+2Z_C - 9)N_{17}$ electrons;

N_{18} ions of $Mn(C_2O_4)_2^{-1} \cdot n_{18}H_2O$ carries $(Z_{Mn} - 3)N_{18}$ manganese electrons and $4(Z_C - 3)N_{18}$ carbon electrons; together $(Z_{Mn}+4Z_C - 15)N_{18}$ electrons;

N_{19} ions of $Mn(C_2O_4)_3^{-3} \cdot n_{19}H_2O$ carries $(Z_{Mn} - 3)N_{19}$ manganese electrons and $6(Z_C - 3)N_{19}$ carbon electrons; together $(Z_{Mn}+ 6Z_C - 21)N_{19}$ electrons;

N_{20} ions of $Mn^{+2} \cdot n_{20}H_2O$ carries $(Z_{Mn} - 2)N_{17}$ manganese electrons;

N_{21} ions of $MnOH^{+1} \cdot n_{21}H_2O$ carries $(Z_{Mn} - 2)N_{21}$ manganese electrons;

N_{22} molecules of $MnSO_4 \cdot n_{22}H_2O$ carries $(Z_{Mn} - 2)N_{22}$ manganese electrons;

N_{23} molecules of $MnC_2O_4 \cdot n_{23}H_2O$ carries $(Z_{Mn} - 2)N_{23}$ manganese electrons and $2(Z_C - 3)N_{23}$ carbon electrons; together $(Z_{Mn}+2Z_C - 8)N_{23}$ electrons;

N_{24} ions of $Mn(C_2O_4)_2^{-2} \cdot n_{24}H_2O$ carries $(Z_{Mn} - 2)N_{24}$ manganese electrons and $4(Z_C - 3)N_{24}$ carbon electrons; together $(Z_{Mn}+4Z_C - 14)N_{24}$ electrons;

N_{25} ions of $Mn(C_2O_4)_3^{-2} \cdot n_{25}H_2O$ carries $(Z_{Mn} - 2)N_{25}$ manganese electrons and $4(Z_C - 3)N_{25}$ carbon electrons; together $(Z_{Mn}+4Z_C - 14)N_{25}$ electrons;

N_{26} ions of $Fe^{+2} \cdot n_{26}H_2O$ carries $(Z_{Fe} - 2)N_{26}$ iron electrons;

N_{27} ions of $FeOH^{+1} \cdot n_{27}H_2O$ carries $(Z_{Fe} - 2)N_{27}$ iron electrons;

N_{28} molecules of $FeSO_4 \cdot n_{28}H_2O$ carries $(Z_{Fe} - 2)N_{28}$ iron electrons;

N_{29} ions of $Fe(C_2O_4)_2^{-2} \cdot n_{29}H_2O$ carries $(Z_{Fe} - 2)N_{29}$ iron electrons and $4(Z_C - 3)N_{29}$ carbon electrons; together $(Z_{Fe}+4Z_C - 14)N_{29}$ electrons;

N_{30} ions of $Fe(C_2O_4)_3^{-4} \cdot n_{30}H_2O$ carries $(Z_{Fe} - 2)N_{30}$ iron electrons and $6(Z_C - 3)N_{30}$ carbon electrons; together $(Z_{Mn}+4Z_C - 14)N_{30}$ electrons;

N_{31} ions of $Fe^{+3} \cdot n_{31}H_2O$ carries $(Z_{Fe} - 3)N_{31}$ iron electrons;

N_{32} ions of $FeOH^{+1} \cdot n_{32}H_2O$ carries $(Z_{Fe} - 3)N_{32}$ iron electrons;

N_{33} ions of $Fe(OH)_2^{+1} \cdot n_{33}H_2O$ carries $(Z_{Fe} - 3)N_{33}$ iron electrons;

N_{34} ions of $Fe_2(OH)_2^{+1} \cdot n_{34}H_2O$ carries $(Z_{Fe} - 3)N_{34}$ iron electrons;

N_{35} ions of $FeSO_4^{+1} \cdot n_{35}H_2O$ carries $(Z_{Fe} - 3)N_{35}$ iron electrons;

N_{36} ions of $Fe(SO_4)_2^{-1} \cdot n_{36}H_2O$ carries $(Z_{Fe} - 3)N_{36}$ iron electrons;

N_{37} ions of $FeC_2O_4^{+1} \cdot n_{37}H_2O$ carries $(Z_{Fe} - 3)N_{37}$ iron electrons and $2(Z_C - 3)N_{37}$ carbon electrons; together $(Z_{Mn}+2Z_C - 9)N_{37}$ electrons;

N_{38} ions of $Fe(C_2O_4)_2^{-1} \cdot n_{38}H_2O$ carries $(Z_{Fe} - 3)N_{38}$ iron electrons and $4(Z_C - 3)N_{38}$ carbon electrons; together $(Z_{Mn}+4Z_C - 15)N_{38}$ electrons;

N_{39} ions of $Fe(C_2O_4)_3^{-3} \cdot n_{39}H_2O$ carries $(Z_{Fe} - 3)N_{39}$ iron electrons and $6(Z_C - 3)N_{39}$ carbon electrons; together $(Z_{Mn}+ 6Z_C - 21)N_{39}$ electrons;

$a_1 \cdot N_{40}$ molecules of **$FeC_2O_4 \cdot n_{40}H_2O$** carries $a_1 \cdot (Z_{Fe} - 2)N_{40}$ iron electrons and $2a_1 \cdot (Z_C - 3)N_{40}$ carbon electrons; together $a_1 \cdot (Z_{Fe}+2Z_C - 8)N_{40}$ electrons;

$a_2 \cdot N_{41}$ molecules of **$MnC_2O_4 \cdot n_{41}H_2O$** carries $a_2 \cdot (Z_{Mn} - 2)N_{41}$ manganese electrons and $2a_2 \cdot (Z_C - 3)N_{41}$ carbon electrons; together $a_2 \cdot (Z_{Fe}+2Z_C - 8)N_{41}$ electrons;

Balancing the electrons brought by 'players' in components and those dissipated between 'players' in the species, we obtain Eq. 19. This way, the equivalence of the Approaches I and II to GEB is proved here.

Linearity properties involved with T and D subsystems

The T subsystem (V): Applying the notations from (9), we have the following balances:

$f_0 = ChB$

$N_2 - N_3 + N_4 - N_{11} - 2N_{12} - N_{13} = 0$

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + 2N_4n_4 + N_{10}(2+2n_{10}) + N_{11}(1+2n_{11}) + 2N_{12}n_{12} + 2N_{13}n_{13} = 2N_{03}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4n_4 + N_{10}(3+n_{10}) + N_{11}(3+n_{11}) + N_{12}(3+n_{12}) + N_{13}(4+n_{13})$

$= 4N_{01} + 2N_{02} + N_{03}$

$f_{12} = 2 \cdot f_2 - f_1$

$- N_2 + N_3 + 4N_{10} + 5N_{11} + 6N_{12} + 8N_{13} = 8N_{01} + 4N_{02}$

$- f_3 = - f(K)$

$N_{01} = N_4$

$-4f_5 = -4f(C)$

$4N_{02} = 4N_{10} + 4N_{11} + 4N_{12}$

$-7f_7 = -7f(Mn)$

$7N_{01} = 7N_{13}$

$f_{12} + f_0 - f_3 - 4f_5 - 7f_7 \qquad (20)$

$0 = 0 \qquad (20a)$

As we see, the linear combination (19) for T, considered as a non-redox system, is transformed into identity (20a) [32].

Formulation of the D subsystem (V_0)

Applying again the notations from (9), we have the following balances:

$f_0 = ChB$

$N_2 - N_3 - N_5 - 2N_6 - N_8 - 2N_9 - N_{11} - 2N_{12} + 2N_{26} + N_{27} - 2N_{29} - 4N_{30} = 0$

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_5(1+2n_5) + 2N_6n_6 + N_7(2+2n_7) + N_8(1+2n_8) + 2N_9n_9 +$

$N_{10}(2+2n_{10}) + N_{11}(1+2n_{11}) + 2N_{12}n_{12} + 2N_{26}n_{26} + N_{27}(1+2n_{27}) + 2N_{28}n_{28} + 2N_{29}n_{29} +$

$2N_{30}n_{30} + 2a_1 \cdot N_{40}n_{40} = 14N_{04} + 6N_{05} + 2N_{06} + 2N_{08}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_5(4+n_5) + N_6(4+n_6) + N_7(4+n_7) + N_8(4+n_8) + N_9(4+n_9) =$

$N_{10}(3+n_{10}) + N_{11}(3+n_{11}) + N_{12}(3+n_{12}) + N_{26}n_{26} + N_{27}(1+n_{27}) + N_{28}(4+n_{28}) + N_{29}(8+n_{29}) +$

$N_{30}(12+n_{30}) + 4a_1 \cdot N_{40}n_{40} = 11N_{04} + 6N_{05} + 4N_{06} + 2N_{07} + N_{08}$

$f_{12} = 2 \cdot f_2 - f_1$

$- N_2 + N_3 + 7N_5 + 8N_6 + 6N_7 + 7N_8 + 8N_9 + 4N_{10} + 5N_{11} + 6N_{12} + N_{27} + 8N_{28} + 16N_{29} +$

$24N_{30} + 6a_1 \cdot N_{40}n_{40} = 8N_{04} + 6N_{06} + 4N_{07}$

$-6f_4 = - 6f(SO_4)$

$$6N_{04} + 6N_{06} = 6N_5 + 6N_6 + 6N_{28}$$

$$-6 \cdot f_{51} = -6 \cdot f(C_2O_4):$$

$$6N_{05} = 6N_7 + 6N_8 + 6N_9 + 12N_{29} + 18N_{30}$$

$$-4 \cdot f_{52} = -4 \cdot f(CO_3):$$

$$4N_{07} = 4N_{10} + 4N_{11} + 4N_{12}$$

$$-2f_6 = -2f(Fe)$$

$$2N_{04} = 2N_{26} + 2N_{27} + 2N_{28} + 2N_{29} + 2N_{30}$$

$$f_{12} + f_0 - 6f_4 - 6 \cdot f_{51} - 4 \cdot f_{52} - 2f_6 \tag{21}$$

$$0 = 0 \tag{21a}$$

As we see, the linear combination (20) for D, considered as a non–redox system, is transformed into identity (21a) [32].

The balances for the D+T system expressed in terms of concentrations

Applying the notations specified above, we have the relations:

$$\left[X_i^{z_i}\right](V_0 + V) = 10^3 \cdot \frac{N_i}{N_A}, \quad CV = 10^3 \cdot \frac{N_{01}}{N_A}, \quad C_1V = 10^3 \cdot \frac{N_{02}}{N_A},$$

$$C_{01}V_0 = 10^3 \cdot \frac{N_{04}}{N_A}, \quad C_{02}V_0 = 10^3 \cdot \frac{N_{05}}{N_A}, \quad C_{03}V_0 = 10^3 \cdot \frac{N_{06}}{N_A}, \quad C_{04}V_0$$

$$= 10^3 \cdot \frac{N_{07}}{N_A} \tag{22}$$

The balances (10) – (15), (17a) written in terms of molar concentrations are as follows:

$$[H^{+1}] - [OH^{-1}] + [K^{+1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] - [HC_2O_4^{-1}] - 2[C_2O_4^{-2}] - [HCO_3^{-1}]$$

$$- 2[CO_3^{-2}] - [MnO_4^{-1}] - 2[MnO_4^{-2}] + 3[Mn^{+3}] + 2[MnOH^{+2}] + [MnC_2O_4^{+1}] - [Mn(C_2O_4)_2^{-1}]$$

$$- 3[Mn(C_2O_4)_3^{-3}] + 2[Mn^{+2}] + [MnOH^{+1}] - 2[Mn(C_2O_4)_2^{-2}] - 4[Mn(C_2O_4)_3^{-4}] + 2[Fe^{+2}] + [FeOH^{+1}]$$

$$- 2[Fe(C_2O_4)_2^{-2}] - 4[Fe(C_2O_4)_3^{-4}] + 3[Fe^{+3}] + 2[FeOH^{+2}] + [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}]$$

$$+ [FeSO_4^{+1}] - [Fe(SO_4)_2^{-1}] + [FeC_2O_4^{+1}] - [Fe(C_2O_4)_2^{-1}] - 3[Fe(C_2O_4)_3^{-3}] = 0 \tag{10a}$$

$$[K^{+1}] = CV/(V_0+V) \tag{11a}$$

$$[HSO_4^{-1}] + [SO_4^{-2}] + [MnSO_4] + [FeSO_4] + [FeSO_4^{+1}] + 2[Fe(SO_4)_2^{-1}] - (C_{01}+C_{03})V_0/(V_0+V) = 0 \tag{12a}$$

$$2([H_2C_2O_4]+[HC_2O_4^{-1}]+[C_2O_4^{-2}]) + ([H_2CO_3]+[HCO_3^{-1}]+[CO_3^{-2}]) + 2[MnC_2O_4^{+1}] + 4[Mn(C_2O_4)_2^{-1}] + 6[Mn(C_2O_4)_3^{-3}] + 2[MnC_2O_4] + 4[Mn(C_2O_4)_2^{-2}] + 6[Mn(C_2O_4)_3^{-4}] + 2[MnC_2O_4] + 4[Mn(C_2O_4)_2^{-2}] + 6[Mn(C_2O_4)_3^{-4}] + 4[Fe(C_2O_4)_2^{-2}] + 6[Fe(C_2O_4)_3^{-4}] + 2[FeC_2O_4^{+1}] + 4[Fe(C_2O_4)_2^{-1}] + 6[Fe(C_2O_4)_3^{-3}] +$$

$$2a_1 \cdot [\mathbf{FeC_2O_4}] + 2a_2 \cdot [\mathbf{MnC_2O_4}] - (2C_{02}V_0 + C_{04}V_0 + C_1V)/(V_0+V) = 0 \tag{13a}$$

$$[Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] + [Fe(C_2O_4)_2^{-2}] + [Fe(C_2O_4)_3^{-4}] + [Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}] + [FeC_2O_4^{+1}] + [Fe(C_2O_4)_2^{-1}] + [Fe(C_2O_4)_3^{-3}] +$$

$$a_1 \cdot [\mathbf{FeC_2O_4}] - C_{01}V_0/(V_0+V) = 0 \tag{14a}$$

$$[MnO4-1] + [MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}] + [MnC_2O_4^{+1}] + [Mn(C_2O_4)_2^{-1}] + [Mn(C_2O_4)_3^{-3}] +$$

$$[Mn^{+2}] + [MnOH^{+1}] + [MnSO_4] + [MnC_2O_4] + [Mn(C_2O_4)_2^{-2}] + [Mn(C_2O_4)_3^{-4}] +$$

$$a_2 \cdot [\mathbf{MnC_2O_4}] - CV/(V_0+V) = 0 \tag{15a}$$

$$- [H^{+1}] + [OH^{-1}] + 7[HSO_4^{-1}] + 8[SO_4^{-2}] + 6[H_2C_2O_4] + 7[HC_2O_4^{-1}] + 8[C_2O_4^{-2}] + 4[H_2CO_3] +$$

$$5[HCO_3^{-1}] + 6[CO_3^{-2}] + 8[MnO_4^{-1}] + 8[MnO_4^{-2}] + [MnOH^{+2}] + 8[MnC_2O_4^{+1}] + 16[Mn(C_2O_4)_2^{-1}] + 24[Mn(C_2O_4)_3^{-3}] + [MnOH^{+1}] + 8[MnSO_4] + 8[MnC_2O_4] + 16[Mn(C_2O_4)_2^{-2}] + 24[Mn(C_2O_4)_3^{-4}] +$$

$$[FeOH^{+1}] + 8[FeSO_4] + 16[Fe(C_2O_4)_2^{-2}] + 24[Fe(C_2O_4)_3^{-4}] + [FeOH^{+2}] + 2[Fe(OH)_2^{+1}] +$$

$$2[Fe_2(OH)_2^{+4}] + 8[FeSO_4^{+1}] + 16[Fe(SO_4)_2^{-1}] + 8[FeC_2O_4^{+1}] + 16[Fe(C_2O_4)_2^{-1}] + 24[Fe(C_2O_4)_3^{-3}] + a_1 \cdot 8[FeC_2O_4] + a_2 \cdot 8[MnC_2O_4]$$

$$- (8C_{01}V_0 + 6C_{02}V_0 + 4C_{04}V_0 + 4C_1V + 6C_{03}V_0) + 8CV)/(V_0+V) = 0 \tag{16b}$$

$$6([H_2C_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) + 4([H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}]) + 7[MnO_4^{-1}] + 6[MnO_4^{-2}] +$$

$$3([Mn^{+3}] + [MnOH^{+2}]) + 9[MnC_2O_4^{+1}] + 15[Mn(C_2O_4)_2^{-1}] + 21[Mn(C_2O_4)_3^{-3}] + 2([Mn^{+2}] + [MnOH^{+1}] + [MnSO_4]) + 8[MnC_2O_4] + 14[Mn(C_2O_4)_2^{-2}] + 20[Mn(C_2O_4)_3^{-4}] + 2([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) + 14[Fe(C_2O_4)_2^{-2}] + 20[Fe(C_2O_4)_3^{-4}] + 3([Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}]) + 9[FeC_2O_4^{+1}] + 15[Fe(C_2O_4)_2^{-1}] + 21[Fe(C_2O_4)_3^{-3}] + a_1 \cdot 8[FeC_2O_4] + a_2 \cdot 8[MnC_2O_4]$$

$$- (2C_{01}V_0 + 6C_{02}V_0 + 4C_{04}V_0 + 7CV + C_1V)/(V_0+V) = 0 \tag{17b}$$

$$2(Z_C - 3)([H_2C_2O_4]+[HC_2O_4^{-1}]+[C_2O_4^{-2}]) + (Z_C - 4)([H_2CO_3]+[HCO_3^{-1}]+[CO_3^{-2}]) +$$

$$(Z_{Fe} - 2)([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) + (Z_{Fe} - 3)([Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}]) +$$

$$2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}]) + (Z_{Mn} - 7)[MnO_4^{-1}] + (Z_{Mn} - 6)[MnO_4^{-2}] +$$

$$(Z_{Mn} - 3)([Mn^{+3}] + [MnOH^{+2}]) + (Z_{Mn} - 2)([Mn^{+2}] + [MnOH^{+1}] + [MnSO_4]) +$$

$$a_1 \cdot (Z_{Fe} + 1 \cdot 2 \cdot Z_C - 8)[FeC_2O_4] + (Z_{Fe}+2 \cdot 2Z_C - 14)[Fe(C_2O_4)_2^{-2}] + (Z_{Fe} + 3 \cdot 2Z_C - 20)[Fe(C_2O_4)_3^{-4}] +$$

$$(Z_{Fe} + 1 \cdot 2 \cdot Z_C - 9)[FeC_2O_4^{+1}] + (Z_{Fe} + 2 \cdot 2 \cdot Z_C - 15)[Fe(C_2O_4)_2^{-1}] + (Z_{Fe} + 3 \cdot 2 \cdot Z_C - 21)[Fe(C_2O_4)_3^{-3}] +$$

$$(Z_{Mn} + 1 \cdot 2Z_C - 8) \cdot ([MnC_2O_4] + a_2 \cdot [\mathbf{MnC_2O_4}]) + (Z_{Mn} + 2 \cdot 2Z_C - 14) \cdot [Mn(C_2O_4)_2^{-2}] +$$

$(Z_{Mn} + 3 \cdot 2Z_C - 20)[Mn(C_2O_4)_3^{-4}] + (Z_{Mn} + 1 \cdot 2Z_C - 9)[MnC_2O_4^{+1}] +$

$(Z_{Mn} + 2 \cdot 2 \cdot Z_C - 15)[Mn(C_2O_4)_2^{-1}] + (Z_{Mn} + 3 \cdot 2 \cdot Z_C - 21)[Mn(C_2O_4)_3^{-3}]$

$- (2(Z_C - 3)C_{02}V_0 + (Z_C - 4)(C_{04}V_0 + C_1V) + (Z_{Fe} - 2)C_{01}V_0 + (Z_{Mn} - 7)CV)/(V_0 + V) = 0 \quad$ (19a)

Some regularities involved with linear combinations of the balances

Equations (16b), (17b) and (19a) are equivalent forms of GEB. Equation (16b) is obtained from the balance (16b), considered as the *pr*imary form of GEB, *pr*-GEB [1]. Equation (19a), obtained also on the basis of prior knowledge of ONs for C, Fe and Mn, is also called as the 'short' version of GEB [1] for this system. Equation (17b) contains components and species composed only of 'players', i.e., where 'fans' are not involved. These 'fans' are cancelled after further combination with balances related to other 'fans'. The relation (11a), where only one species is involved, is considered as equality, not equation; it can enter immediately the charge balance (10a). The volume V of T added from the start up to a defined point of the titration, is the current parameter (not variable), from the viewpoint of the calculation procedure.

Equation (17b) and, consequently, Equation (19a) includes only the components and species where 'players' are involved. The equivalent forms: (16b), (17b), (19a) of GEB have different notation lengths. One can, however, reduce the length of this notation, making further, linear combination of $f_{12} + f_0 - f_3 - 6f_4$ (Equation 17a) with f_5, f_6 and f_7 (Equations 13-16, resp.). After addition of (17a) to the balances (13b) – (15b) :

$-4f_5 = -4f(C)$

$8N_{05} + 4(N_{02} + N_{07}) = 8(N_7 + N_8 + N_9) + 4(N_{10} + N_{11} + N_{12}) + 8N_{17} + 16N_{18} + 24N_{19} + 8N_{23}$

$+ 16N_{24} + 24N_{25} + 16N_{29} + 24N_{30} + 8N_{37} + 16N_{38} + 24N_{39} + 8a_1 \cdot N_{40} + 8a_2 \cdot N_{41}$ (13b)

$-3f_6 = -3f(Fe)$

$3N_{04} = 3(N_{26} + N_{27} + N_{28}) + 3N_{29} + 3N_{30} + 3(N_{31} + N_{32} + N_{33} + 2N_{34} + N_{35} + N_{36}) + 3N_{37} + 3N_{38} + 3N_{39} + a_1 \cdot 3N_{40}$ (14b)

$-2f_7 = -2f(Mn)$

$2N_{01} = 2N_{13} + 2N_{14} + 2(N_{15} + N_{16}) + 2N_{17} + 2N_{18} + 2N_{19} + 2(N_{20} + N_{21} + N_{22}) + 2N_{23} + 2N_{24} +$

$2N_{25} + a_2 \cdot 2N_{41}$ (15b)

and further rearrangements the terms, we get the simplest (in this respect) combination

$f_{12} + f_0 - f_3 - 6f_4 - 4f_5 - 2f_6 - 2f_7$ (23)

$N_{04} + 2N_{05} + 5N_{13} + 4N_{14} + N_{15} + N_{16} = 2(N_7 + N_8 + N_9) + N_{17} + 3N_{18} + 5N_{19} + 2N_{23} + 4N_{24} + 6N_{25} +$

$(N_{26} + N_{27} + N_{28}) + 5N_{29} + 7N_{30} + 2N_{37} + 4N_{38} + 6N_{39} + a_1 \cdot 3N_{40} + a_2 \cdot 2N_{41} = 5N_{01} \quad \Rightarrow$

$2(N_7 + N_8 + N_9) + (N_{26} + N_{27} + N_{28}) - (5N_{13} + 4N_{14} + N_{15} + N_{16}) + N_{17} + 3N_{18} + 5N_{19} + 2N_{23} + 4N_{24} +$

$6N_{25} + 5N_{29} + 7N_{30} + 2N_{37} + 4N_{38} + 6N_{39} + a_1 \cdot 3N_{40} + a_2 \cdot 2N_{41} = 2N_{05} + N_{04} - 5N_{01} \quad \Rightarrow$ (23a)

$2([H_2C_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) + ([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) - (5[MnO_4^{-1}] + 4[MnO_4^{-2}] +$

$[Mn^{+3}] + [MnOH^{+2}]) + [MnC_2O_4^{+1}] + 3[Mn(C_2O_4)_2^{-1}] + 5[Mn(C_2O_4)_3^{-3}] + 2([MnC_2O_4] + a_2 \cdot [\mathbf{MnC_2O_4}]) + 4[Mn(C_2O_4)_2^{-2}] + 6[Mn(C_2O_4)_3^{-4}] + a_1 \cdot 3[\mathbf{FeC_2O_4}] + 5[Fe(C_2O_4)_2^{-2}] + 7[Fe(C_2O_4)_3^{-4}] +$

$2[FeC_2O_4^{+1}] + 4[Fe(C_2O_4)_2^{-1}] + 6[Fe(C_2O_4)_3^{-3}] = \dfrac{2C_{02}V_0 + C_{01}V_0 - 5CV}{V_0 + V}$

(23b)

On the calculation procedure

Concentrations of the species in Equations (10a) – (15a), (19a) are also interrelated in the set of independent expressions for equilibrium constants, found e.g. in [53-55]. Altogether, 29 independent equilibrium constants are involved in the computer program, presented in Appendix for the D+T system with 41 species. Among others, the relationships for solubility products of the precipitates: $\mathbf{FeC_2O_4}$ and $\mathbf{MnC_2O_4}$ pre-assumed in the model are as follows:

$K_{so1} = [Fe^{+2}][C_2O_4^{-2}]$ ($pK_{so1} = 6.7$), $K_{so2} = [Mn^{+2}][C_2O_4^{-2}]$ ($pK_{so2} = 5.3$).

The complete set of independent equilibrium constants provides all quantitative knowledge on the system in question. Some qualitative knowledge on the system in question is also valuable; this kind of knowledge is particularly desired in the case of metastable systems.

Six independent variables:

$x(1) = pH$, $x(2) = E$,

$x(3) = - \log[Mn^{+2}]$ or $x(3) = - \log[MnC_2O_4]$,

$x(4) = - \log[Fe^{+2}]$ or $x(4) = - \log[FeC_2O_4]$,

$x(5) = - \log[H_2C_2O_4]$, $x(6) = - \log[SO_4^{-2}]$

are involved in the set of six independent equations: (9a), (11a), (12a), (13a), (14a) and (17b) in the computer program. The volume V of titrant T is the current (operating) parameter in the related algorithm.

Concentrations of particular species are presented there without parentheses. Some exemplary concentrations are denoted as follows:

$[Fe^{+3}] = Fe3$, $[MnOH^{+2}] = Mn3OH$, $[MnO_4^{-1}] = Mn7O4$, $[MnO_4^{-2}] = Mn6O4$, $[Fe(C_2O_4)_3^{-4}] = Fe2C2O43$,

$pr1 = [FeC_2O_4]$, $pr2 = [MnC_2O_4]$, $logpr1 = log[FeC_2O_4]$. At the pre-assumed concentrations of components in D and T,

indicated in legend for figure 1, the solubility products of both precipitates are not crossed, i.e., FeC_2O_4 and MnC_2O_4 are not formed. Precipitation of **MnO_2** is not possible too, because of the low pH value and high buffer capacity of the mixture, resulting from presence of an excess of H_2SO_4.

Conclusions

The example presented above provides some general regularities, obligatory for all electrolytic systems, in aqueous media, and extended on non-aqueous and mixed-solvent media, with amphiprotic (co)solvent(s) included. These regularities can be listed from different viewpoints.

The criterion distinguishing between redox and non-redox systems

The simplest/shortest form of GEB (Equations 23a, 23b) related to D+T mixture as the redox system is different from identity, $0 = 0$. This way, the linear independency of f_{12} from other balances: $f_0, f_3, f_4, f_5, f_6, f_7$ is proved here. The identity property, $0 = 0$, was stated for T (19, 19a) and D (20, 20a), considered as non-redox (sub)systems, i.e., f_{12} is linearly

dependent on: f_0, f_3, f_5, f_7 (for T) or $f_0, f_4, f_{51}, f_{52}, f_6$ (for D), see [32]. This confirms the general regularity stated within GATES that :

f_{12} is linearly dependent on $f_0, f_3, \ldots, f_K$ for all non-redox systems, of any degree of complexity; consequently, non-redox systems are fully described with use of K − 1 balances f_0, $f_3, \ldots, f_K$, i.e., the balances for H and O: $f_1 = f(H)$ and $f_2 = f(O)$ and then $f_{12} = 2 \cdot f_2 − f_1$ are not applied for description of non-redox systems;

f_{12} is linearly independent on $f_0, f_3, \ldots, f_K$ for all redox systems, of any degree of complexity; consequently, redox systems are fully described with use of K balances $f_0, f_{12}, f_3, \ldots, f_K$; the balance $f_{12} = 2 \cdot f_2 − f_1$ is the basis to formulation of GEB, completing the set of independent equations needed for description of redox systems;

the GEB completing the set of equations needed for description of a redox system can be obtained according to two equivalent approaches, named as Approach I to GEB and Approach II to GEB;
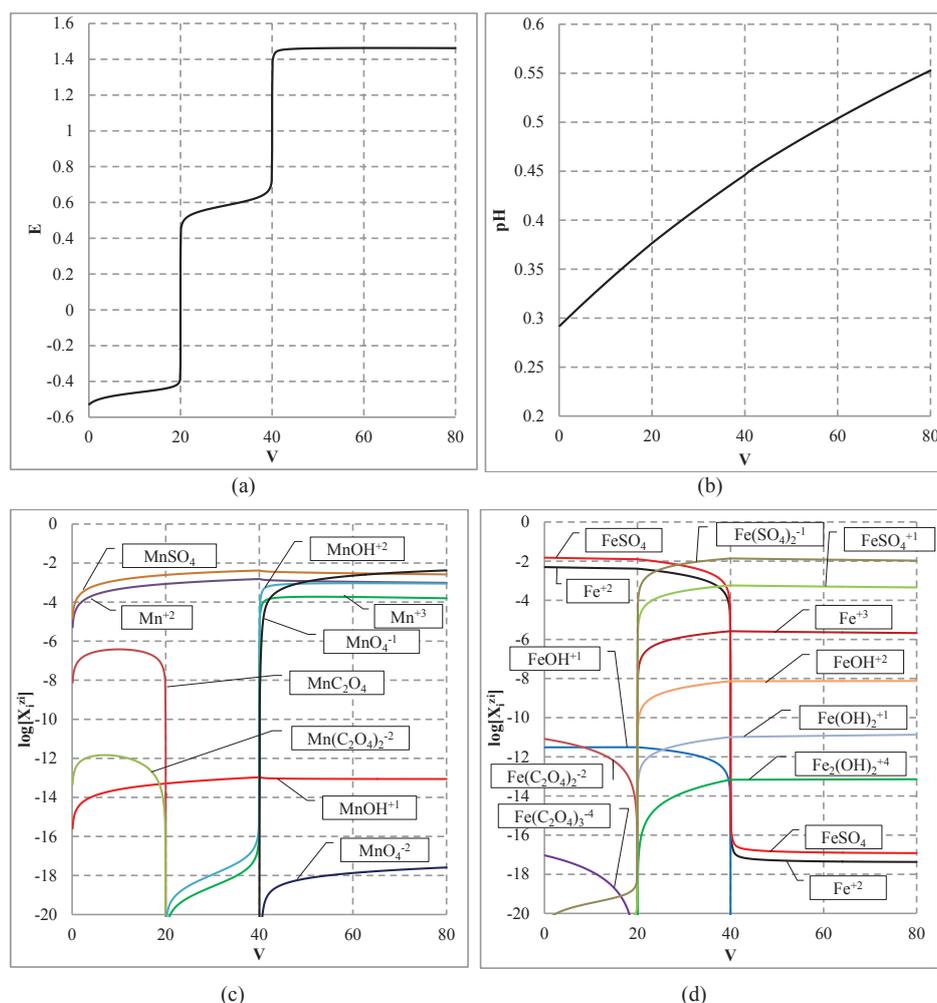

Figure 1: The (a) E = E(V), (b) pH = pH(V) relationships and dynamic speciation diagrams for (c) Mn- and (d) Fe- species, plotted at $V_0 = 100$, $C_{01} = 0.02$, $C_{02} = 0.01$, $C = 0.02$, $C_{03} = 0.5$; $C_1 = C_{04} = 0.001$.

$C_{01} = 0.02, C_{02} = 0.01$			
V [mL]	E [V]	V [mL]	E [V]
19.5	-0.4124	39.5	0.6791
19.6	-0.4094	39.6	0.6849
19.7	-0.4056	39.7	0.6925
19.8	-0.4003	39.8	0.7030
19.9	-0.3913	39.9	0.7209
20	-0.2177	40	1.0529
20.1	0.4475	40.1	1.3872
20.2	0.4654	40.2	1.4052
20.3	0.4760	40.3	1.4158
20.4	0.4835	40.4	1.4233
20.5	0.4893	40.5	1.4290

the linear independency or dependency of f_{12} from $f_0, f_3, \ldots, f_K$ is the general criterion distinguishing between redox and non-redox systems.

Oxidation numbers (ONs)

The Approach I to GEB needs prior knowledge of ONs for 'players' involved in components and species of the system; ONs of elements in 'fans' are not taken into account there;

Within the Approach I to GEB, all components and species with 'players' are distinguished and collected; 'fans' are not considered on the step of GEB formulation according to Approach I;

The terms oxidant(s) and reductant(s) are not applied (are derivative terms) on the step of formulation of a redox system according to Approaches I and II. This fact is of capital importance, when redox equilibria involved e.g., with complex organic species, are considered.

The Approach II to GEB needs none prior knowledge of ONs for elements in components and species; the terms: 'players' and 'fans', oxidant and reductant are not indicated; full 'democracy' is provided within the Approach II to GEB. Known (or pre-assumed) composition of a species, expressed by its formula, together with external charge of this species, provides an information sufficient to formulate the related balances.

The linear combination of balances as the source of ONs

Linear combination of charge and elemental/core balances suggested/practiced above was aimed at finding the simplest form of a linear combination, in the sense of the minimizing the number of kinds of different components.

Let us refer to linear combinations of linear combinations of balances related to the non-redox systems (D, T) and the redox system (D+T). Applying the notation suggested in (4), (5), (6a) and (6b), we rewrite (20) and (21) as follows.

For non-redox subsystem T

$$f_{12} + f_0 - f_3 - 4f_5 - 7f_7 = 0 \quad \Rightarrow \quad 1 \cdot (+1)f_1 + 1 \cdot (-2)f_2$$
$$+ 1 \cdot (+1)f_3 + 1 \cdot (+4)f_5 + 1 \cdot (+7)f_7 = f_0 \Rightarrow$$

$$1 \cdot (+1)f(H) + 1 \cdot (-2)f(O) + 1 \cdot (+1)f(K) + 1 \cdot (+4)f(CO_3) + 1 \cdot (+7)f(MnO_4) = ChB \tag{20b}$$

For non-redox subsystem D

$$f_{12} + f_0 - 6f_4 - 6 \cdot f_{51} - 4 \cdot f_{52} - 2f_6 = 0 \quad \Rightarrow$$

$$1 \cdot (+1)f_1 + 1 \cdot (-2)f_2 + 1 \cdot (+6)f_4 + 2 \cdot (+3)f_{51} + 1 \cdot (+4)f_{52} + 1 \cdot (+2)f_6 = f_0 \Rightarrow$$

$$1 \cdot (+1)f(H) + 1 \cdot (-2)f(O) + 1 \cdot (+6)f(SO_4) + 2 \cdot (+3)f(C_2O_4) + 1 \cdot (+4)f(CO_3) + 1 \cdot (+2)f(Fe) = ChB \tag{21b}$$

In both subsystems, all 'fans' are involved. The coefficients at particular balances in the related linear combinations are equal to the product of: a number of elements in the related entities (component, species) and the ON of the element in these entities.

For the redox D+T system

linear combination of balances for 'fans' of this system (Equation 17) can be rearranged as follows:

$$f_{12} + f_0 - f_3 - 6f_4 = 0 \quad \Rightarrow \quad 1 \cdot (+1)f_1 + 1 \cdot (-2)f_2 + 1 \cdot (+1)f_3 + 1 \cdot (+6)f_4 = f_0 \Rightarrow$$

$$1 \cdot (+1)f(H) + 1 \cdot (-2)f(O) + 1 \cdot (+1)f(K) + 1 \cdot (+6)f(SO_4) = ChB \tag{17c}$$

A remark. Some subsystems of other D + T systems may have redox properties. This is the case, for example, in D of D + T system, where (a) NaOH solution as T is added to: Br_2 or HBrO, solution [43,44], as D, or (b) HCl solution as T is added into NaIO solution [23,24]. Redox properties result there from disproportionating of the solute (Br_2, HBrO, NaIO) dissolved in water.

The elemental versus core balances

Unlike the D + T system, where oxalate species are transformed into carbonate species, in D they exist side by side, without mutual transformation. Therefore, oxalate and carbonate species in D can be placed in separate balances, only for an illustrative confirmation of the f_{12} properties of dependency in non-redox systems. In D+T system, the carbonate species as products of the reaction (8) and that resulting from the admixtures in D and T, are included in one, joint balance for f_c. Writing the common balance $f_5 = 2f_{51} + f_{52}$ is a matter of choice for D, but the necessity for D+T.

The element S enters the related system only as a core SO_4^{-2}, and then the balances: $f(S)$ and $f(SO_4)$ for the related systems are identical.

Further reference to the 'card game'

Let us recall again the 'card game' with 'players', 'fans' and 'money', presented in ref [1]. (pp. 41-43).

As usually happens in the card game practice, the players devote to the game only a part of their cash resources. Similarly, in redox reactions may participate electrons from the valence shells of atoms of electron–active elements; the electrons from the valence shell of the reductant atoms are transferred onto the valence shell of the oxidant atoms. However, this restriction to the valence electrons is not required here. For example, one can replace Z_C by ζ_C ($Z_C < \zeta_C$), Z_{Fe} by ζ_{Fe} ($Z_{Fe} < \zeta_{Fe}$) and Z_{Mn} by ζ_{Mn} ($Z_{Mn} < \zeta_{Mn}$) in Equation 19. In particular, we can put in there $\zeta_X = \zeta_X = 0$ for X = C, Fe, Mn. Obviously, we get here the relation identical with Equation 17a.

This way, we recall the card game without 'live cash' but with 'debt of honor' – in not accidental reference to the title of the thriller novel by T. Clancy; btw, the "Debt of honor" was published in 1994, like the papers [43-45].

Final comments

A keystone for the overall, thermodynamic knowledge on electrolytic systems is the linear combination $2 \cdot f(O) - f(H)$ of elemental balances: $f(H)$ for H and $f(O)$ for O, that can be formulated both for non–redox and redox systems, in aqueous, non–aqueous and mixed-solvent systems, with amphiprotic (co)solvent(s) involved. In any redox system, the $2 \cdot f(O) - f(H)$ is linearly independent on ChB and other, elemental/core balances, for For any non–redox system, $2 \cdot f(O) - f(H)$ is linearly dependent on those balances. The equation for $2 \cdot f(O) - f(H)$, considered as the *primary* form of GEB, $p - \text{GEB} = 2 \cdot f(O) - f(H)$, is the basis of GEB formulation for redox systems according to Approach II to GEB. 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.

The number of electron–active elements ('players') in a redox system, considered according to GATES/ GEB principles, is practically unlimited; among others, the systems with one, two, three or four 'players' were considered.

All earlier (dated from 1960s) trials made towards formulation of electrolytic redox systems were only clumsy attempts of resolution of the problem in question, as stated in [10–12]. Those approaches were slavishly related to the stoichiometric reaction notations, involving only two pairs of indicated species participating in redox reaction; there were usually minor species of the system considered. The species different from those involved in the reaction notation were thus omitted in considerations. What is more, the charge balance and concentration balances for accompanying substances were also omitted. Theoretical considerations were related to virtual cases, not to real, electrolytic redox systems. The computer simulation realized within GATES with use of iterative computer programs, e.g. MATLAB, provides quite a new quality in knowledge gaining. It enables to follow the details of the process, registered with use of measurable quantities, such as pH and/or potential E.

All the inferences made within GATES/GEB are based on firm, mathematical (algebraic) foundations, not on an extremely "fragile" chemical notation principle that is only a faint imitation of a true, algebraic notation [21,30]. The approach proposed allows to understand far better all physicochemical phenomena occurring in the system in question and improve some methods of analysis. All the facts testify very well about the potency of simulated calculations made, according to GATES, on the basis of all attainable physicochemical knowledge. Testing the complex redox and non–redox systems with use of iterative computer programs deserves wider popularization among physicochemists and chemists–analysts.

Epilogue

In the fourteenth century, William of Ockham has formulated the parsimony (economy of thinking) [50], principle that "entities should not be multiplied unnecessarily'' ("*Pluralitas non est ponenda sine neccesitate*''), known briefly as "Ockham's razor". In reference to science, it means that simpler theories are generally better than more complex ones. GATES, based on fundamental rules of the matter conservation, acts according to the Ockham razor principle.

The Approach II to GEB shows immediately that the equivalent equations for GEB are derived from the common root of the elements conservation and then GEB is fully compatible with charge and concentration balances, like "the lotus flower, lotus leaf and lotus seed come from the same root" [7]. This compatibility is directly visible from the viewpoint of the Approach II to GEB. The GEB, based on a reliable law of the matter conservation, is equally robust as equations for charge and concentration balances. The complementarity of the GEB (Approaches I and II) to other balances is regarded as the expression of Harmony of Nature, and GATES/GEB as an example of excellent epistemological paradigm.

References

1. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Generalized Electron Balance (GEB) as the Law of Nature in Electrolytic Redox Systems, in: Redox: Principles and Advanced Applications, Ali Khalid MA, (Ed.) In Tech Chap 2: 9-55. **Link:** https://bit.ly/2Yj9tZF

2. Michałowski T (2011) Application of GATES and MATLAB for Resolution of Equilibrium, Metastable and Non-Equilibrium Electrolytic Systems, Chapter 1 (1-34) in: Applications of MATLAB in Science and Engineering (ed. Michałowski T), InTech - Open Access publisher in the fields of Science, Technology and Medicine, InTech Janeza Trdine 9, 51000 Rijeka, Croatia.

3. Michałowska-Kaczmarczyk AM, Michałowski T (2014) GATES as the Unique Tool for Simulation of Electrolytic Redox and Non-Redox Systems. J Anal Bioanal Tech 5: 204. **Link:** https://bit.ly/2Ygqdwl

4. Michałowski T, Pietrzyk A (2006) A thermodynamic study of struvite+water system. Talanta 68: 594-601. **Link:** https://bit.ly/2LHSxpv

5. Michałowski T, Asuero AG (2012) Thermodynamic modelling of dolomite behavior in aqueous media. Journal of Thermodynamics 2012: 12. **Link:** https://bit.ly/32VWHiX

6. Michałowski T, Michałowska-Kaczmarczyk AM, Toporek M (2013) Formulation of general criterion distinguishing between non-redox and redox systems. Electrochimica Acta 112: 199-211. **Link:** https://bit.ly/2JxGwAG

7. Michałowski T, Toporek M., Michałowska-Kaczmarczyk AM, Asuero AG (2013) New Trends in Studies on Electrolytic Redox Systems. Electrochimica Acta 109: 519–531. **Link:** https://bit.ly/2JOe390

8. Michałowska-Kaczmarczyk AM, Toporek M, Michałowski T (2015) Speciation Diagrams in Dynamic Iodide + Dichromate System, Electrochimica Acta 155: 217–227. **Link:** https://bit.ly/2xPNfPP

9. Toporek M, Michałowska-Kaczmarczyk AM, Michałowski T (2015) Symproportionation versus Disproportionation in Bromine Redox Systems. Electrochimica Acta 171: 176–187. Link : https://bit.ly/2ObxJJp

10. Michałowski T (2010) The Generalized Approach to Electrolytic Systems: I. Physicochemical and Analytical Implications. Critical Reviews in Analytical Chemistry 40: 2-16. **Link:** https://bit.ly/2LOu0zt

11. Michałowski T, Pietrzyk A, Ponikvar-Svet, M, Rymanowski M (2010) The Generalized Approach to Electrolytic Systems: II. The Generalized Equivalent Mass (GEM) Concept. Critical Reviews in Analytical Chemistry 40: 17-29. **Link:** https://bit.ly/2GuHc8j

12. Michałowska-Kaczmarczyk AM, Asuero AG, Michałowski T (2015) "Why not stoichiometry" versus "Stoichiometry – why not?" Part I. General context. Critical Reviews in Analytical Chemistry 45: 166–188. **Link:** https://bit.ly/2YicYvf

13. Michałowska-Kaczmarczyk AM, Asuero AG, Toporek M, Michałowski T (2015) "Why not stoichiometry" versus "Stoichiometry – why not?" Part II. GATES in context with redox systems. Critical Reviews in Analytical Chemistry 45: 240–268. **Link:** https://bit.ly/2GvYTEn

14. Michałowska-Kaczmarczyk AM, Michałowski T, Toporek M, Asuero AG (2015) "Why not stoichiometry" versus "Stoichiometry – why not?" Part III, Extension of GATES/GEB on Complex Dynamic Redox Systems. Critical Reviews in Analytical Chemistry 45: 348-366. **Link:** https://bit.ly/2XMHJgv

15. Michałowska-Kaczmarczyk AM, Michałowski T (2014) Compact formulation of redox systems according to GATES/GEB principles. Journal of Analytical Sciences, Methods and Instrumentation 4: 39-45. **Link:** https://bit.ly/2YqkTL2

16. Toporek M, Michałowska-Kaczmarczyk AM, Michałowski T (2014) Disproportionation Reactions of HIO and NaIO in Static and Dynamic Systems. American Journal of Analytical Chemistry 5: 1046-1056. **Link:** https://bit.ly/2K6brDl

17. Michałowska-Kaczmarczyk AM, Michałowski T, Toporek M (2016) Formulation of Dynamic Redox Systems according to GATES/GEB Principles. International Journal of Electrochemical Science 11: 2560-2578. **Link:** https://bit.ly/2JGroA8

18. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017). A general property differentiating between redox and non-redox electrolytic systems and its consequences. International Journal of Mathematics and Statistics Invention 6: 67-76. **Link:** https://bit.ly/2YgGVM5

19. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Formulation of simple electrolytic redox systems according to GATES/GEB principles, Journal of Chemistry and Applied Chemical Engineering 1: 1-10. **Link:** https://bit.ly/32SF5EB

20. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Oxidation number, oxidant and reductant as derivative concepts within GATES/GEB formulation. Journal of Chemistry and Applied Chemical Engineering 1: 2. **Link:** https://bit.ly/2JRZbHA

21. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Dynamic Buffer Capacities in Redox Systems. Journal of Chemistry and Applied Chemical Engineering 1: 1 - 7. **Link:** https://bit.ly/2Y8CtUs

22. Michałowski T, Ponikvar-Svet M, Asuero AG, Kupiec K (2012) Thermodynamic and kinetic effects involved with pH titration of As(III) with iodine in a buffered malonate system. Journal of Solution Chemistry 41: 436-446. **Link:** https://bit.ly/2SKHCMz

23. Meija J, Michałowska-Kaczmarczyk AM, Michałowski T (2017) Redox titration challenge. Analytical and Bioanalytical Chemistry 409: 11−13. **Link:** https://bit.ly/2LV6UpU

24. Michałowski T, Michałowska-Kaczmarczyk AM, Meija J (2017) Solution of redox titration challenge. Analytical and Bioanalytical Chemistry 409: 4113-4115. **Link:** https://bit.ly/2GvLImJ

25. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Some Regularities Involved with Oxidation Numbers Stated in Formulation of Redox Systems According to GATES/GEB Principles. Journal of Analytical, Bioanalytical and Separation Techniques 2: 102-110. **Link:** https://bit.ly/2xLx46d

26. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) General Properties of the Balances 2·f(O)-f(H) Related to Electrolytic Systems. Analytical Chemistry: An Indian Journal 17(2): 124. **Link:** https://bit.ly/2JUxiyU

27. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Principles of Titrimetric Analyses According to Generalized Approach to Electrolytic Systems (GATES), in: Advances in Titration Techniques, Vu Dang Hoang (Ed.) InTech Chap 5: 133-171. **Link:** https://bit.ly/2OkWHFZ

28. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2018) The balance 2·f(O) − f(H) as a keystone in formulation of electrolytic systems. Research and Reviews in Computational Chemistry 1: 1-9. **Link:** https://bit.ly/2Ym7dwD

29. Michałowska-Kaczmarczyk AM, Michałowski T (2018) The Balance 2·f(O) − f(H) as a Cornerstone in Formulation of Electrolytic Systems. Journal of New Developments in Chemistry 2: 1-13. **Link:** https://bit.ly/2YclTkU

30. Michałowska-Kaczmarczyk AM, Michałowski T (2018) The importance of linear algebra in theory of electrolytic systems. Austin Chemical Engineering 5: 1060.

31. Michałowska-Kaczmarczyk AM, Michałowski T (2018) "The distinguishing role of 2·f(O) - f(H) in electrolytic systems". Biomedical Journal of Scientific & Technical Research 8: 1-10. **Link:** https://bit.ly/2GqCyIv

32. Michałowska-Kaczmarczyk AM, Michałowski T (2013) Comparative balancing of non-redox and redox electrolytic systems and its consequences. American Journal of Analytical Chemistry 4: 46-53. **Link:** https://bit.ly/30Zrc5I

33. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Some Regularities Involved with Oxidation Numbers Stated in Formulation of Redox Systems According to GATES/GEB Principles. Journal of Analytical, Bioanalytical and Separation Techniques 2: 102-110. **Link:** https://bit.ly/2xLx46d

34. Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Oxidation number, oxidant and reductant as derivative concepts within GATES/GEB formulation. Journal of Chemistry and Applied Chemical Engineering 1:2. **Link:** https://bit.ly/2JRZbHA

35. Michałowski T (ed) (2011) Applications of MATLAB in Science and Engineering. InTech - Open Access publisher in the fields of Science, Technology and Medicine. Link: https://bit.ly/2JypmDe

36. Pereira E (ed) (2010) Matlab − Modeling, Programming and Simulations, Sciyo, Rijeka, Croatia. **Link:** https://bit.ly/2LJ5Sy2

37. Michałowska-Kaczmarczyk AM, Michałowski T (2014) Generalized Electron Balance for Dynamic Redox Systems in Mixed-Solvent Media, Journal of Analytical Sciences, Methods and Instrumentation 4: 102-109.

38. Michałowska-Kaczmarczyk AM, Michałowski T (2014) Linear Dependence of Balances for Non-Redox Electrolytic Systems. American Journal of Analytical Chemistry 5: 1285-1289. **Link:** https://bit.ly/2JTTd9u

39. Michałowski T, Pilarski B, Asuero AG, Michałowska-Kaczmarczyk AM (2014) Modeling of Acid-Base Properties in Binary-Solvent Systems, Chap. 9.4:

623-648 in "Handbook of Solvents", Vol. 1 Properties, Wypych, G. (Editor), ChemTec Publishing, Toronto.

40. Michałowski T, Pilarski B, Asuero AG, Michałowska-Kaczmarczyk AM (2019) Modeling of Acid-Base Properties in Binary-Solvent Systems, Chap. 9.4: 665-690 in "Handbook of Solvents", Vol. 1 Properties, Wypych G (Editor), ChemTec Publishing, 3rd Edition, Toronto.

41. Michałowski T (2018) Generalized Electron Balance (GEB) as the Law of Nature for electrolytic redox systems, keynote lecture in: International Conference on Analytical Chemistry, Madrid, Spain 21-22. **Link:** https://bit.ly/2Yj9tZF

42. Michałowski T, Lesiak A (1993) Graphical presentation of redox titrimetric data, Euroanalysis VIII, Edinburgh, UK. September 5-11.

43. Michalowski T (1994) Calculation of pH and potential E for bromine aqueous solutions. Journal of Chemical Education 71: 560-562. **Link:** https://bit.ly/2LlDeCY

44. Michałowski T, Lesiak A (1994) Acid-base titration curves in disproportionating redox systems. Journal of Chemical Education 71: 632-636. **Link:** https://bit.ly/2xLvql2

45. Michałowski T, Lesiak A (1994) Formulation of generalized equations for redox titration curves. Chemia Analityczna (Warsaw) 39: 623-637. **Link:** https://bit.ly/2Yblgdi

46. Michałowski, T, Wajda N, Janecki D (1996) A Unified Quantitative Approach to Electrolytic Systems. Chemia Analityczna (Warsaw) 41: 667-685. **Link:** https://bit.ly/2Y6Ucvn

47. Michałowski T, Rymanowski M, Pietrzyk A (2005) Non-typical Brönsted's acids and bases. Journal of Chemical Education 82: 470-472. **Link:** https://bit.ly/32W0igX

48. Michałowski T, Baterowicz A, Madej A, Kochana J (2001) An extended Gran method and its applicability for simultaneous determination of Fe(II) and Fe(III). Analytica Chimica Acta 442: 287-293. **Link:** https://bit.ly/2JS7Wl2

49. Michałowski T, Toporek M, Rymanowski M (2005) Overview on the Gran and other linearization methods applied in titrimetric analyses. Talanta 65: 1241-1253. **Link:** https://bit.ly/2SMThKY

50. Michałowski T (2007) Complementarity of physical and chemical laws of preservation in aspect of electrolytic systems (in Polish). Wiadomości Chemiczne 61: 625-640.

51. Michałowski T, Kupiec K, Rymanowski M (2008) Numerical analysis of the Gran methods. A comparative study. Analytica Chimica Acta 606: 172-183. **Link:** https://bit.ly/32seHRR

52. Ponikvar M, Michałowski T, Kupiec K, Wybraniec S, Rymanowski M (2008) Experimental verification of the modified Gran methods applicable to redox systems. Analytica Chimica Acta 628: 181-189. **Link:** https://bit.ly/2yfvwl3

53. Lurie Ju (1975) Handbook of Analytical Chemistry, Mir Publishers, Moscow. **Link:** https://bit.ly/2yfXHk1

54. Inczédy J (1976) Analytical Applications of Complex Equilibria, Horwood, Chichester. **Link:** https://bit.ly/2YqBHkV

55. Kotrlý S, Šůcha L (1985) Handbook of chemical equilibria in analytical chemistry, Ellis Horwood Limited, Halsted Press, John Wiley & Sons, New York, p. 248. **Link:** https://bit.ly/32NXZg5