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Research Article

General properties of the balance $2 \cdot f(O) - f(H)$ in electrolytic systems some detailed remarks on elemental versus core balances

Abstract

Any electrolytic system in aqueous media is described with use of charge balance, $f_0 = \text{ChB}$, and K elemental or core balances, $f_k = f(Y_k)$ ($k = 1, \dots, K$). The balances: $f_1 = f(H)$ and $f_2 = f(O)$ are the basis to formulate the linear combination $f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(O) - f(H)$. For a redox system with $K - K^*$ electron-active elements (players), f_{12} is linearly independent on f_0, f_3, \dots, f_K , i.e., the redox system is described by K independent balances $f_0, f_{12}, f_3, \dots, f_K$. For a non-redox system ($K^* = K$), f_{12} is linearly dependent on f_0, f_3, \dots, f_K , i.e., a redox system is described by $K - 1$ independent balances f_0, f_3, \dots, f_K . Consequently, the linear combination $f_{12} + f_0 \Leftrightarrow \sum_{k=3}^{K^*} d_k \cdot f_k - f_0 \Leftrightarrow \sum_{k=3}^{K^*} d_k \cdot f_k - f_0$ with d_k equal to the oxidation numbers of the related elements, is reducible to identity, $0 = 0$, for a non-redox system, i.e., f_{12} is not the independent balance in this system. In a redox system, f_{12} is the primary form of generalized electron balance (GEB). The paper is completed by description of typical redox and non-redox systems according to GATES/GEB principles.

Introduction

The article concerns fundamental regularities, obligatory for electrolytic systems of different complexity, considered from the viewpoint of Generalized Approach to Electrolytic Systems (GATES), formulated by Michałowski (1992) [1,2]. According to GATES, a balancing of any electrolytic system is based on rules of conservation of particular elements, and on a charge balance, expressing the rule of electroneutrality of this system. We refer to aqueous media, $W = \text{H}_2\text{O}$, where the species $X_i^{Z_i}$ exist as hydrates $X_i^{Z_i} \cdot n_i W$; $z_i = 0, \pm 1, \pm 2, \dots$ is a charge, expressed in elementary charge units, $e = F/NA$ ($F = \text{Faraday's constant}$, $NA = \text{Avogadro's number}$, $n_i = n_i W = n_i \text{H}_2\text{O} \geq 0$ is a mean number of water ($W = \text{H}_2\text{O}$) molecules attached to $X_i^{Z_i}$. For ordering purposes, we assume $Y_1 = \text{H}$ (hydrogen) and $Y_2 = \text{O}$ (oxygen), and formulate first the linear combination

$$f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(O) - f(H) \quad (1)$$

Of elemental balances: $f_1 = f(H)$ for hydrogen (H) and $f_2 = f(O)$ for oxygen (O), related to the system considered. Then the linear combination of f_{12} with charge balance (f_0) and elemental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) for elements/cores $Y_k \neq \text{H, O}$ will be formulated [3]. A core is considered as a

cluster of different atoms with defined composition (expressed by chemical formula), structure and external charge, e.g. SO_4^{2-} is a core with external charge -2 , composed of two elements: S and O. The balances f_k ($k=1, \dots, K$) interrelate the numbers of different elements/cores in components forming a system, and in the species thus formed. The notation of the balances (f_0, f_1, \dots, f_K) applied here is as follows

$$f_k = \{s_{ik}\} - \{c_{jk}\} = 0 \Leftrightarrow -f_k = \{c_{jk}\} - \{s_{ik}\} = 0 \Leftrightarrow f_k : \{s_{ik}\} = \{c_{jk}\} \Leftrightarrow -f_k : \{c_{jk}\} = \{s_{ik}\} \quad (2)$$

where $\{c_{jk}\}$ is referred to a set of some components, $\{s_{ik}\}$ – to some species in k -th balance; $c_{i0} = 0$, i.e., $\{c_{i0}\} = \emptyset$ (empty set, for f_0). Numbers of components of j -th kind are denoted by N_{0j} ($j=1, \dots, J$), numbers of the species $s_{ik} = X_i^{Z_i}$ of i -th kind are denoted by N_i ($i=1, \dots, I$). For balancing purposes, the hydrated species $X_i^{Z_i} \cdot n_i W$ in the system are specified as $X_i^{Z_i}$ (N_i, n_i); e.g., the notation $\text{HSO}_4^{-1} (N_5, n_5)$ applied in Example 1 (below) refers to N_5 ions of $\text{HSO}_4^{-1} \cdot n_5 \text{H}_2\text{O}$ involving: $N_5(1+2n_5)$ atoms of H, $N_5(4+n_5)$ atoms of O, and N_5 atoms of S. Molar concentration of the species $X_i^{Z_i} \cdot n_i W$ be denoted by $X_i^{Z_i}$.

The f_{12} (Equation 1) is the primary form of Generalized Electron Balance (GEB), $f_{12} = \text{pr-GEB}$, formulated (2005) for redox systems according to Approach II to GEB, where prior knowledge of ONs of all elements in components and species is not needed. The Approach II to GEB is fully compatible with the Approach I to GEB [4-15] formulated (1992) and based on the principle of common pool of electrons involved with electron-active elements, named as 'players' and distinguished from electron-non-active elements considered as 'fans', when a redox system is considered according to card game principle [15]; ONs for elements in components and species are needed in the Approach I. The principles of GEB formulation, discovered (1992, 2005) by Michałowski and resolved according to Generalized Approach to Electrolytic Systems (GATES) as GATES/GEB [1,16], were unknown in earlier literature.

GEB completes the set of K balances ($f_0, f_{12}, f_3, \dots, f_K$) as algebraic equations necessary for solving a redox system; $K-1$ balances (f_0, f_3, \dots, f_K) are required for solving a non-redox system; f_{12} is omitted as derivative (not primary) balance. GEB is the law of Nature related to equilibrium, metastable or kinetic electrolytic redox systems, of any degree of complexity [1,15-24].

In this paper, the general properties of the linear combination of the balances ($f_0, f_{12}, f_3, \dots, f_K$) related to non-redox and redox systems of different degree of complexity, are discussed. Any redox system is involved with change of oxidation numbers of $K - K^*$ electron-active elements (players), where K^* is the number of electron-non-active elements (fans). For a non-redox system we have $K^*=K$, i.e., $K - K^* = 0$. Assuming that H and O participate the system as fans, we formulate the linear combination [15,16,25-33].

$$f_{12} + f_0 - \sum_{K=3}^{K^*} d_k \cdot f_k \quad 0 \Leftrightarrow \quad \sum_{K=3}^{K^*} d_k \cdot f_k - f_k = 0 \quad (3)$$

applicable for non-redox and redox systems, of different degree of complexity. For a non-redox system

$$\sum_{K=1}^{K^*} d_k \cdot f_k - f_k \quad (3a)$$

is transformed into identity, $0 = 0$. We prove that the equation (3)

(10) implies a general criterion distinguishing between non-redox and redox systems;

(20) defines d_k as oxidation numbers (ONs) of particular elements in components and species of a non-redox or redox system.

Synthesis of chemical and physical laws of conservation is expressed, respectively, by the equalities of left and right sides of Equations (3) and (3a).

Formulation of non-redox systems

Example 1. The (static) system is formed from the following components: $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (N_{01}), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (N_{02}) (Sal

Mirabilis), H_2O (N_{03}). The species in the system thus formed, namely:

H_2O (N_1), H^{+1} (N_2 , n_2), OH^{-1} (N_3 , n_3), Na^{+1} (N_4 , n_4), HSO_4^{-1} (N_5 , n_5), SO_4^{-2} (N_6 , n_6), H_2S (N_7 , n_7),

HS^{-1} (N_8 , n_8), S^{-2} (N_9 , n_9)

are involved in the following balances:

$f_0 = \text{ChB}$:

$$N_2 - N_3 + N_4 - N_5 - 2N_6 - N_8 - 2N_9 = 0$$

$f_1 = f(\text{H})$:

$$\begin{aligned} & 2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + 2N_4n_4 + N_5(1+2n_5) + \\ & 2N_6n_6 + N_7(2+2n_7) + N_8(1+2n_8) + 2N_9n_9 \\ & = 18N_{01} + 20N_{02} + 2N_{03} \end{aligned}$$

$f_2 = f(\text{O})$:

$$\begin{aligned} & N_1 + N_2n_2 + N_3(1+n_3) + N_4n_4 + N_5(4+n_5) + N_6(4+n_6) + \\ & N_7n_7 + N_8n_8 + N_9n_9 \\ & = 9N_{01} + 14N_{02} + N_{03} \end{aligned}$$

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

$$= N_2 + N_3 + 7N_5 + 8N_6 - 2N_7 - N_8 = 8N_{02}$$

$-f_3 = -f(\text{Na})$:

$$2N_{01} + 2N_{02} = N_4$$

$-6 \cdot f_4 = 6 \cdot f(\text{SO}_4)$:

$$6N_{02} = 6N_5 + 6N_6$$

$2 \cdot f_5 = 2 \cdot f(\text{S})$:

$$2N_7 + 2N_8 + 2N_9 = 2N_{01}$$

$$f_{12} + f_0 - f_3 - 6 \cdot f_4 + 2 \cdot f_5 \quad (4)$$

$$0 = 0$$

i.e., the linear combination (4) is transformed into identity; it can be rewritten into the form

$$(+1) \cdot f_1 + (-2) \cdot f_2 + (+1) \cdot f_3 + (+6) \cdot f_4 + (-2) \cdot f_5 - f_0 = 0 \quad \Leftrightarrow$$

$$(+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+1) \cdot f(\text{Na}) + (+6) \cdot f(\text{SO}_4) + (-2) \cdot f(\text{S}) - \text{ChB} \quad (5)$$

where the numbers in round brackets as multipliers for f_i ($i=1, \dots, 5$) are equal to ONs of the related elements. Within f_{12} , and then within (5), N_1 and all n_{iW} values, within components and species, are cancelled. The species $X_1^{Z_1} \cdot n_{iW}$ not involving H and/or O within $X_1^{Z_1}$, are also cancelled within f_{12} . More specifically, the f_3 involving only one kind of species, is considered here as equality, not as equation.

In this system, symproportionation [21] of sulfur does not

occur; from this viewpoint, the system is at a metastable state [1,13]. Consequently, all elements (H, O, Na, S) involved in this system are perceived as fans, i.e., $K^* = K = 4$. Sulfide oxidation can occur in presence of sulfate-reducing bacteria [34]. Sulfide gives sulfate after oxidation with H_2O_2 [35], whereas sulfate ions are not reducible in usual procedure [36].

The elemental balance for S is $f^*(S) = f_4 = f_4 + f_5$. The linear combination

$$f_{12} + f_0 - f_3 + p \cdot f_{45} \quad (6)$$

is not transformable into identity $0 = 0$, at any p -value. From (6) and (4) we get the contradiction $p = 6$ and $p = -2$, i.e., f_{45} is not applicable for checking f_{12} (Eq. 1) as the criterion of independency of the related balances.

Example 2 (dynamic system). V_0 mL of titrand (D), containing $ZnSO_4$ (C0) + NH_3 (C1) + NH_4Cl (C2) + NaH_2In (erio T, C0In) is titrated with V mL of titrant (T) containing EDTA (C) [3].

The D is composed of N_{01} molecules of $ZnSO_4 \cdot 7H_2O$ (goslarite), 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 the 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 , at defined point of titration (V mL of T added). In the D+T system, the following species are formed:

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}).

In particular, the complex $ZnOHL^{-3}$ is formed from $ZnOH^{+1}$ and L^{-4} .

The charge (ChB), elemental ($f(H)$, $f(O)$, $f(Zn)$, $f(Cl)$, $f(Na)$) and core ($f(SO_4)$, $f(NH_3)$, $f(C_{20}H_{10}N_3O_7S)$, $f(C_{10}H_{12}N_2O_8)$) balances are written here as follows:

$$f_0 = ChB :$$

$$N_2 - N_3 - N_4 - 2N_5 - N_6 + N_7 + N_8 + 2N_{10} + N_{11} - N_{13} - 2N_{14} + 2N_{15} + 2N_{16} + 2N_{17} + 2N_{18} + N_{19} - N_{22} - 2N_{23}$$

$$- 3N_{24} - N_{25} - 4N_{26} + 2N_{27} + N_{28} - N_{30} - 2N_{31} - 3N_{32} - 4N_{33} - N_{34} - 2N_{35} - 3N_{36} = 0$$

$$f_1 = f(H) :$$

$$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + N_4(1 + 2n_4) + 2N_5n_5 + 2N_6n_6 + 2N_7n_7 + N_8(4 + 2n_8) + N_9(3 + 2n_9) + 2N_{10}n_{10}$$

$$+ N_{11}(1 + 2n_{11}) + N_{12}(2 + 2n_{12}) + N_{13}(3 + 2n_{13}) + N_{14}(4 + 2n_{14}) + N_{15}(3 + 2n_{15}) + N_{16}(6 + 2n_{16}) + N_{17}(9 + 2n_{17})$$

$$+ N_{18}(12 + 2n_{18}) + 2N_{19}n_{19} + 2N_{20}n_{20} + N_{21}(13 + 2n_{21}) + N_{22}(12 + 2n_{22}) + N_{23}(11 + 2n_{23}) + N_{24}(10 + 2n_{24})$$

$$+ N_{25}(10 + 2n_{25}) + N_{26}(20 + 2n_{26}) + N_{27}(18 + 2n_{27}) + N_{28}(17 + 2n_{28}) + N_{29}(16 + 2n_{29}) + N_{30}(15 + 2n_{30})$$

$$+ N_{31}(14 + 2n_{31}) + N_{32}(13 + 2n_{32}) + N_{33}(12 + 2n_{33}) + N_{34}(13 + 2n_{34}) + N_{35}(12 + 2n_{35}) + N_{36}(13 + 2n_{36})$$

$$= 14N_{01} + 3N_{02} + 4N_{03} + 12N_{04} + 2N_{05} + 18N_{06} + 2N_{07}$$

$$f_2 = f(O) :$$

$$N_1 + N_2n_2 + N_3(1 + n_3) + N_4(4 + n_4) + N_5(4 + n_5) + N_6n_6 + N_7n_7 + N_8n_8 + N_9n_9 + N_{10}n_{10}$$

$$+ N_{11}(1 + n_{11}) + N_{12}(2 + n_{12}) + N_{13}(3 + n_{13}) + N_{14}(4 + n_{14}) + N_{15}n_{15} + N_{16}n_{16} + N_{17}n_{17}$$

$$+ N_{18}n_{18} + N_{19}n_{19} + N_{20}(4 + n_{20}) + N_{21}(7 + n_{21}) + N_{22}(7 + n_{22}) + N_{23}(7 + n_{23}) + N_{24}(7 + n_{24})$$

$$+ N_{25}(7 + n_{25}) + N_{26}(14 + n_{26}) + N_{27}(8 + n_{27}) + N_{28}(8 + n_{28}) + N_{29}(8 + n_{29}) + N_{30}(8 + n_{30})$$

$$+ N_{31}(8 + n_{31}) + N_{32}(8 + n_{32}) + N_{33}(8 + n_{33}) + N_{34}(8 + n_{34}) + N_{35}(8 + n_{35}) + N_{36}(9 + n_{36})$$

$$= 11N_{01} + 7N_{04} + N_{05} + 10N_{06} + N_{07}$$

$$- 2 \cdot f_3 = - 2 \cdot f(Zn)$$

$$2N_{01} = 2N_{10} + 2N_{11} + 2N_{12} + 2N_{13} + 2N_{14} + 2N_{15} + 2N_{16} + 2N_{17} + 2N_{18} + 2N_{19} + 2N_{20} + 2N_{25} + 2N_{26}$$

$$+ 2N_{34} + 2N_{35} + 2N_{36}$$

$$f_4 = f(Cl) :$$

$$N_6 + N_{19} = N_{03}$$

$$- f_5 = - f(Na) :$$

$$N_{04} + 2N_{06} = N_7 \quad (7)$$

$$- 6 \cdot f_6 = - 6 \cdot f(SO_4) :$$

$$6N_{01} = 6N_4 + 6N_5 + 6N_{20}$$

$$3 \cdot f_7 = 3 \cdot f(NH_3) :$$

$$3N_8 + 3N_9 + 3N_{15} + 6N_{16} + 9N_{17} + 12N_{18} = 3N_{02} + 3N_{03}$$

$$- f_8 = - f(C_{20}H_{10}N_3O_7S) :$$

$$N_{04} = N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + 2N_{26} \quad (8)$$

$$0 \cdot f_9 = 0 \cdot f(C_{10}H_{12}N_2O_8) :$$

$$0 \cdot N_{27} + 0 \cdot N_{28} + 0 \cdot N_{29} + 0 \cdot N_{30} + 0 \cdot N_{31} + 0 \cdot N_{32} + 0 \cdot N_{33} + 0 \cdot N_{34} + 0 \cdot N_{35} + 0 \cdot N_{36} = 0 \cdot N_{06} \quad (9)$$

The balance

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

$$- N_2 + N_3 + 7N_4 + 8N_5 - 4N_8 - 3N_9 + N_{11} + 2N_{12} + 3N_{13} + 4N_{14} - 3N_{15} - 6N_{16} - 9N_{17} - 12N_{18} + 8N_{20} + N_{21}$$

$$+ 2N_{22} + 3N_{23} + 4N_{24} + 4N_{25} + 8N_{26} - 2N_{27} - N_{28} + N_{30} + 2N_{31} + 3N_{32} + 4N_{33} + 3N_{34} + 4N_{35} + 5N_{36}$$

$$= 8N_{01} - 3N_{02} - 4N_{03} + 2N_{04} + 2N_{06}$$

$$f_0 + f_{12} - 2 \cdot f_3 + f_4 - f_5 - 6 \cdot f_6 + 3 \cdot f_7 - f_8 + 0 \cdot f_9 \quad (10)$$

$$0 = 0$$

i.e., the the linear combination (10) is transformed into identity, $0 = 0$. It can be rewritten into the form

$$(+1) \cdot f_1 + (-2) \cdot f_2 + (+2) \cdot f_3 + (-1) \cdot f_4 + (+1) \cdot f_5 + (+6) \cdot f_6 + (-3) \cdot f_7 + (+1) \cdot f_8 + (0) \cdot f_9 - f_0 = 0 \quad (11)$$

i.e. the numbers in round brackets as multipliers for f_i ($i=1, \dots, 9$) are equal to ONs of the elements or charges ascribed to S in SO_4^{2-} , N in NH_3 , $C_{20}N_3S$ in all the species of erio T, $C_{10}N_2$ in all the species of EDTA.

This system needs some further comments. All elements (H, O, Na, Cl, Zn, S, N, C) in involved in the components and species the system are considered as fans, i.e., $K^* = K = 8$. The number, 8, of the elements is lower than the total number of charge and elemental/core balances ($K=1+9=10$).

The formula $C_{20}H_{13}N_3O_7S$ for the neutral species of erio T can be rewritten into the form $(C_{20}N_3S)(H_{13}O_7) \Leftrightarrow (C_{20}N_3S)_1(H_2O)_6OH$. The group of elements within $C_{20}N_3S$ has the net charge x calculated from the equation $1 \cdot x + 6 \cdot (0) + 1 \cdot (-2+1) = 0 \Rightarrow x=+1$. Similarly, in $C_{10}H_{16}N_2O_8 = (C_{10}N_2)(H_{16}O_8) = (C_{10}N_2)_1(H_2O)_8$, the net charge x of the $C_{10}N_2$ group is calculated from the equation $1 \cdot x + 8 \cdot 0 = 0$, i.e., $x = 0$. The $C_{20}N_3S+1$ and $C_{10}N_2$ can be also (optionally) considered as cores.

The f_6, f_7, f_8, f_9 are specified separately, for different cores: SO_4^{2-} , NH_3 , $C_{20}H_{10}N_3O_7S-3$, $C_{10}H_{12}N_2O_8-4$, resp. Note that S enters the compounds and species in f_6, f_8 ; N enters the compounds and species in f_7, f_8, f_9 ; C enters the compounds and species in f_8, f_9 . Furthermore, none transformations occur between the cores of the species belonging to separate concentration balances.

Referring again to the species involved with erio T, one can write the elemental balances: $N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + 2N_{26} = N_{04}$ (for S); $3N_{21} + 3N_{22} + 3N_{23} + 3N_{24} + 3N_{25} + 6N_{26} = 3N_{04}$ (for N); $20N_{21} + 20N_{22} + 20N_{23} + 20N_{24} + 20N_{25} + 40N_{26} = 20N_{04}$ (for C). All the equations are identical and equivalent to Eq. (8), because the core $C_{20}H_{10}N_3O_7S$ is unchanged in reactions occurred during the titration. Similarly, the species involved with EDTA fulfill the relations: $10N_{27} +$

$10N_{28} + 10N_{29} + 10N_{30} + 10N_{31} + 10N_{32} + 10N_{33} + 10N_{34} + 10N_{35} + 10N_{36} = 10N_{06}$ (for C), and $3N_{27} + 3N_{28} + 3N_{29} + 3N_{30} + 3N_{31} + 3N_{32} + 3N_{33} + 3N_{34} + 3N_{35} + 3N_{36} = 3N_{06}$ (for N). Both equations are equivalent to f_9 , Eq. (9).

Denoting the elemental balances for S, N and C as $f^*(S) = f_{68}$, $f(N) = f_{789}$, $f(C) = f_{89}$, we have the relations, expressed in the matrix form as follows

$$\begin{bmatrix} f_{68} \\ f_{789} \\ f_{89} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 3 & 2 \\ 0 & 0 & 20 & 10 \end{bmatrix} \begin{bmatrix} f_6 \\ f_7 \\ f_8 \\ f_9 \end{bmatrix}$$

One can prove that the linear combination

$$f_0 + f_{12} - 2 \cdot f_3 + f_4 - f_5 + p \cdot f_{68} + q \cdot f_{789} + r \cdot f_{89} \quad (12)$$

is not transformable into identity $0 = 0$, at any of the (p, q, r) values. Namely, from Equations (10) and (12) we get

$$p(f_6 + f_8) + q(f_7 + 3f_8 + 2f_9) + r(20f_8 + 10f_9) = p \cdot f_6 + q \cdot f_7 + (p+3q+20r) \cdot f_8 + (2q+10r) \cdot f_9 \quad (13)$$

$$- 6 \cdot f_6 + 3 \cdot f_7 - f_8 + 0 \cdot f_9 \Rightarrow p = -6, q = 3, \text{ and } p+3q+20r = -1, 2q+10r = 0 \Rightarrow$$

$$r = (-1 - (-6) - 3 \cdot 3)/20 = -0.2; r = -2 \cdot 3/10 = -0.6.$$

The $r = -0.2$ and $r = -0.6$ are contradictory values. Then the option given by Eq. 12, with f_{68}, f_{789}, f_{89} , is not applicable for checking f_{12} (Eq. 1) as the criterion of independency of the related balances.

Formulation of redox systems

Example 3. We consider here

(10) T subsystem (volume V mL), composed of $KMnO_4$ (N_{01}) + H_2O (N_{02}) + CO_2 (N_{03});

(20) D subsystem (V_0 mL), composed of $FeSO_4 \cdot 7H_2O$ (N_{04}) + H_2SO_4 (N_{05}) + H_2O (N_{06}) + CO_2 (N_{07});

and

(30) D+T redox system (V_0+V mL), as the mixture of D and T, where the following species are formed:

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), H_2CO_3 (N_6, n_6), HCO_3-1 (N_7, n_7),

CO_3-2 (N_8, n_8), $Fe+2$ (N_9, n_9), $FeOH+1$ (N_{10}, n_{10}), $FeSO_4$ (N_{11}, n_{11}), $Fe+3$ (N_{12}, n_{12}), $FeOH+2$ (N_{13}, n_{13}),

$Fe(OH)_2+1$ (N_{14}, n_{14}), $Fe_2(OH)_2+4$ (N_{15}, n_{15}); $FeSO_4+1$ (N_{16}, n_{16}), $Fe(SO_4)_2-1$ (N_{17}, n_{17}), $K+1$ (N_{18}, n_{18}),

MnO_4-1 (N_{19}, n_{19}), MnO_4-2 (N_{20}, n_{20}), $Mn+3$ (N_{21}, n_{21}), $MnOH+2$ (N_{22}, n_{22}), $Mn+2$ (N_{23}, n_{23}), $MnOH+1$ (N_{24}, n_{24}), $MnSO_4$ (N_{25}, n_{25}) .

(14)

The presence of CO_2 in T and D is considered here as an admixture from air, to imitate real conditions of the analysis, on the step of preparation of D and T; the titration $T(V) \Rightarrow$

D(V₀) is realized in the closed system, under isothermal conditions. Precipitation of MnO₂ does not occur at sufficiently low pH value [1].

The D+T dynamic redox system is then composed of non-redox static subsystems: D and T. On this basis, some general properties involved with non-redox and redox systems will be indicated. Different forms of GEB, resulting from linear combinations of charge and elemental balances related to D+T system, will be obtained.

To avoid (possible) disturbances, the common notation (subscripts) assumed in the set (14) of species will be applied for components and species in T, D and D+T. In context with the dynamic D+T system, T and D are considered as static (sub) systems.

Linear combination of balances

The T subsystem

We get here the balances:

$$f_0 = \text{ChB} :$$

$$N_2 - N_3 - N_7 - 2N_8 + N_{18} - N_{19} = 0$$

$$f_1 = f(\text{H}) :$$

$$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_{18}n_{18} + 2N_{19}n_{19} = 2N_02$$

$$f_2 = f(\text{O}) :$$

$$N_1 + N_2n_2 + N_3(1+n_3) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_{18}n_{18} + N_{19}(4+n_{19})$$

$$= 4N_01 + N_02 + 2N_03$$

$$-4 \cdot f_3 = -4 \cdot f(\text{CO}_3) :$$

$$4N_03 = 4N_6 + 4N_7 + 4N_8$$

$$-f_4 = -f(\text{K}) :$$

$$N_01 = N_{18}$$

$$-7 \cdot f_5 = -7 \cdot f(\text{Mn}) :$$

$$7N_01 = 7N_{19}$$

$$f_{12} = 2f_2 - f_1 = 2f(\text{O}) - f(\text{H})$$

$$-N_2 + N_3 + 4N_6 + 5N_7 + 6N_8 + 8N_{19} = 8N_01 + 4N_03$$

$$f_{12} + f_0 - 4f_3 - f_4 - 7f_5 = 0 \Leftrightarrow (+1) \cdot f_1 + (-2) \cdot f_2 + (+4) \cdot f_3 + (+1) \cdot f_4 + (+7) \cdot f_5 - f_0 = 0 \Leftrightarrow$$

$$(+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+4) \cdot f(\text{CO}_3) + (+1) \cdot f(\text{K}) + (+7) \cdot f(\text{Mn}) - \text{ChB} = 0 \quad (15)$$

$$0 = 0$$

i.e., the the linear combination (15) is transformed into

identity, $0 = 0$. The coefficients/multipliers at the balances $f(\text{Y}_k)$ are equal to ONs of elements in the corresponding species.

The D subsystem

We get here the balances:

$$f_0 = \text{ChB}$$

$$N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 2N_9 + N_{10} = 0$$

$$f_1 = f(\text{H})$$

$$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_9n_9 +$$

$$N_{10}(1+2n_{10}) + 2N_{11}n_{11} = 14N_04 + 2N_05 + 2N_06$$

$$f_2 = f(\text{O})$$

$$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_9n_9 +$$

$$N_{10}(1+n_{10}) + N_{11}(4+n_{11}) = 11N_04 + 4N_05 + N_06 + 2N_07$$

$$-4 \cdot f_3 = -4 \cdot f(\text{CO}_3)$$

$$4N_07 = 4N_6 + 4N_7 + 4N_8$$

$$-6 \cdot f_6 = -6 \cdot f(\text{SO}_4)$$

$$6N_04 + 6N_05 = 6N_4 + 6N_5 + 6N_{11}$$

$$-2 \cdot f_7 = -2 \cdot f(\text{Fe})$$

$$2N_04 = 2N_9 + 2N_{10} + 2N_{11}$$

$$f_{12} + f_0 - 4 \cdot f_3 - 6 \cdot f_6 - 2 \cdot f_7 \quad (16)$$

$$0 = 0$$

i.e., the the linear combination (16) is transformed into identity, $0 = 0$. From transformation of (16)

$$(+1) \cdot f_1 + (-2) \cdot f_2 + (+4) \cdot f_3 + (+6) \cdot f_6 + (+2) \cdot f_7 - f_0 \Leftrightarrow$$

$$(+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+4) \cdot f(\text{CO}_3) + (+6) \cdot f(\text{SO}_4) + (+2) \cdot f(\text{Fe}) - \text{ChB} \quad (17)$$

we see again that the coefficients/multipliers at the balances $f(\text{Y}_k)$ are equal to ONs of elements in the corresponding species.

The D+T system

For the D+T system, from (14) we have the balances:

$$f_0 = \text{ChB}$$

$$N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 2N_9 + N_{10} + 3N_{12} + 2N_{13} + N_{14} + 4N_{15} + N_{16} - N_{17} + N_{18} - N_{19} - 2N_{20} +$$

$$3N_{21} + 2N_{22} + 2N_{23} + N_{24} = 0 \quad (18)$$

$$f_1 = f(\text{H})$$

$$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_9n_9 +$$

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

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

$$= 2N_{02} + 4N_{04} + 2N_{05} + 2N_{06}$$

$$f_2 = f(O)$$

$$N_1 + N_{2n_2} + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_9n_9 +$$

$$N_{10}(1+n_{10}) + N_{11}(4+n_{11}) + N_{12}n_{12} + N_{13}(1+n_{13}) + N_{14}(2+n_{14}) + N_{15}(2+n_{15}) + N_{16}(4+n_{16}) + N_{17}(8+n_{17}) +$$

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

$$= 4N_{01} + N_{02} + 2N_{03} + 11N_{04} + 4N_{05} + N_{06} + 2N_{07}$$

$$- 4 \cdot f_3 = - 4 \cdot f(CO_3)$$

$$4N_{03} + 4N_{07} = 4N_6 + 4N_7 + 4N_8 \quad (19)$$

$$- f_4 = - f(K) :$$

$$N_{01} = N_{18} \quad (20)$$

$$- f_5 = - f(Mn)$$

$$N_{01} = N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} \quad (21)$$

$$- 6 \cdot f_6 = - 6 \cdot f(SO_4)$$

$$6N_{04} + 6N_{05} = 6N_4 + 6N_5 + 6N_{11} + 6N_{16} + 12N_{17} + 6N_{25} \quad (22)$$

$$- f_7 = - f(Fe)$$

$$N_{04} = N_9 + N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17} \quad (23)$$

Then we have, by turns,

$$f_{12} = 2 \cdot f(O) - f(H) : \quad (24)$$

$$- N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} + N_{13} + 2N_{14} + 2N_{15} + 8N_{16} + 16N_{17} +$$

$$8N_{19} + 8N_{20} + N_{22} + N_{24} + 8N_{25} = 8N_{01} + 4N_{03} + 8N_{04} + 6N_{05} + 4N_{07} \quad (25)$$

$$f_{12} + f_0 - 4 \cdot f_3 - f_4 - 6 \cdot f_6 \quad (26)$$

$$2(N_9 + N_{10} + N_{11}) + 3(N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17}) + 7N_{19} + 6N_{20} + 3(N_{21} + N_{22}) +$$

$$2(N_{23} + N_{24} + N_{25}) = 7N_{01} + 2N_{04} \quad (27)$$

From transformation of (26) we have

$$(+1) \cdot f_1 + (-2) \cdot f_2 + (+4) \cdot f_3 + (+1) \cdot f_4 + (+6) \cdot f_6 - f_0 \Rightarrow$$

$$(+1) \cdot f(H) + (-2) \cdot f(O) + (+4) \cdot f(CO_3) + (+1) \cdot f(K) + (+6) \cdot f(SO_4) - ChB \quad (28)$$

We see that the coefficients/multipliers at the related balances f_k ($k=1,2,3,4,6$) are equal to ONs of elements in the corresponding species; the balances f_k in (28) are related to fans.

Applying the relations:

$$[X_i^{Z_i}] \cdot (V_0 + V) = 103 \cdot Ni/NA, CV = 103 \cdot N_{01}/NA, CoVo = 103 \cdot N_{04}/NA, C1V = 103 \cdot N_{03}/NA,$$

$$Co1Vo = 103 \cdot N_{05}/NA, Co2Vo = 103 \cdot N_{07}/NA \quad (29)$$

we rewrite Eq. (26) in the more explicit form as

$$2([Fe+2] + [FeOH+1] + [FeSO_4]) + 3([Fe+3] + [FeOH+2] + [Fe(OH)_{2+1}] + 2[Fe_2(OH)_{2+4}] + [FeSO_4+1] + [Fe(SO_4)_{2-1}])$$

$$+ 7[MnO_{4-1}] + 6[MnO_{4-2}] + 3([Mn+3] + [MnOH+2]) + 2([Mn+2] + [MnOH+1] + [MnSO_4])$$

$$= (7CV + 2CoVo)/(V_0 + V) \quad (30)$$

Eq. (30), obtained from (25,28,29), consists only of the species, where players are involved. Other linear combinations were also used. Applying atomic numbers: $ZMn = 25$ and $ZFe = 26$, we have

$$ZFe \cdot f_7 + ZMn \cdot f_5 - (f_{12} + f_0 - 4 \cdot f_3 - f_4 - 6 \cdot f_6) : \quad (31)$$

$$(ZFe-2) \cdot (N_9 + N_{10} + N_{11}) + (ZFe-3) \cdot (N_{12} + N_{13} + N_{14} + 2N_{15}$$

$$+ N_{16} + N_{17}) + (ZMn-7) \cdot N_{19} + (ZMn-6) \cdot N_{20}$$

$$+ (ZMn-3) \cdot (N_{21} + N_{22}) + (ZMn-2) \cdot (N_{23} + N_{24} + N_{25}) = (ZFe-2) \cdot N_{04} + (ZMn-7) \cdot N_{01} \quad \Leftrightarrow$$

$$(ZFe-2) \cdot ([Fe+2] + [FeOH+1] + [FeSO_4]) + (ZFe-3) \cdot ([Fe+3] + [FeOH+2] + [Fe(OH)_{2+1}] + 2[Fe_2(OH)_{2+4}] + [FeSO_4+1] + [Fe(SO_4)_{2-1}]) + (ZMn-7) \cdot [MnO_{4-1}] + (ZMn-6) \cdot [MnO_{4-2}] + (ZMn-3) \cdot ([Mn+3] + [MnOH+2]) +$$

$$(ZMn-2) \cdot ([Mn+2] + [MnOH+1] + [MnSO_4]) = ((ZFe-2) \cdot CoVo + (ZMn-7) \cdot CV)/(V_0 + V) \quad (32)$$

Equation (32) results innediately from the Approach I to GEB, see [6].

The least extended (the most compact) form is as follows [8,25]

$$3 \cdot f_7 + 2 \cdot f_5 - (f_{12} + f_0 - 4 \cdot f_3 - f_4 - 6 \cdot f_6) :$$

$$(N_9 + N_{10} + N_{11}) - (5N_{19} + 4N_{20} + N_{21} + N_{22}) = N_{04} - 5N_{01} \quad \Leftrightarrow$$

$$[Fe+2] + [FeOH+1] + [FeSO_4] - (5[MnO_{4-1}] + 4[MnO_{4-2}] + [Mn+3] + [MnOH+2])$$

$$= (CoVo - 5 \cdot CV)/(V_0 + V) \quad (33)$$

Eq. (25) for f_{12} (24), considered as pr-GEB (Eq. 1), can also be rewritten in terms of concentrations; we have

$$- [H+1] + [OH-1] + 7[HSO_4-1] + 8[SO_4-2] + 4[H_2CO_3] +$$

$$5[\text{HCO}_3^-] + 6[\text{CO}_3^{2-}] + [\text{FeOH}^+] + 8[\text{FeSO}_4] +$$

$$[\text{FeOH}^{2+}] + 2[\text{Fe}(\text{OH})_2] + 8[\text{Fe}(\text{SO}_4)] + 16[\text{Fe}(\text{SO}_4)_2] +$$

$$+ 8[\text{MnO}_4^-] + 8[\text{MnO}_4^{2-}] + [\text{MnOH}^{2+}] + [\text{MnOH}^+] +$$

$$+ 8[\text{MnSO}_4] = (8\text{CV} + 8\text{CoVo} + 4\text{C}_1\text{V} + 6\text{Co}_1\text{Vo} + 4\text{Co}_2\text{Vo}) /$$

$$(\text{Vo} + \text{V}) \quad (34)$$

Equations 30, 32 – 34 are equivalent forms of GEB for this system. Other linear combinations of the balances are also admitted/possible for this purpose; none of them are reduced to the identity $0 = 0$. However, the shortest Eq. (33), chosen arbitrarily, seems to be the most useful for calculation purposes – for obvious reasons.

A comment. In section 3.1.3, the T (section 3.1.1) and D (section 3.1.2) are non-redox subsystems of the redox D+T system (section 3.1.3); this is not the general regularity, of course. In some other systems, D or T or both (D and T) can form redox subsystems. For example, the Br₂ solution considered in [5,6,37,38] is the redox subsystem D; I₂ + KI solution is the redox subsystem T in [39].

Calculation procedure for the D+T system

Completing the set of independent balances

Equation 33 is completed by charge and concentration balances, obtained from Equations 18, 19, 21, 22, 23 and relations (29). We have, by turns,

$$[\text{H}^+] - [\text{OH}^-] - [\text{HSO}_4^-] - 2[\text{SO}_4^{2-}] - [\text{HCO}_3^-] -$$

$$2[\text{CO}_3^{2-}] + 2[\text{Fe}^{2+}] + [\text{FeOH}^+] + 3[\text{Fe}^{3+}] + 2[\text{FeOH}^{2+}] +$$

$$[\text{Fe}(\text{OH})_2] + 4[\text{Fe}_2(\text{OH})_2] + [\text{FeSO}_4] - [\text{Fe}(\text{SO}_4)_2] +$$

$$[\text{K}^+] - [\text{MnO}_4^-] -$$

$$2[\text{MnO}_4^{2-}] + 3[\text{Mn}^{3+}] + 2[\text{MnOH}^{2+}] + 2[\text{Mn}^{2+}] + [\text{MnOH}^+] = 0 \quad (18a)$$

$$[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] - (\text{Co}_2\text{Vo} + \text{C}_1\text{V}) / (\text{Vo} + \text{V}) = 0 \quad (19a)$$

$$[\text{MnO}_4^-] + [\text{MnO}_4^{2-}] + [\text{Mn}^{3+}] + [\text{MnOH}^{2+}] + [\text{Mn}^{2+}] +$$

$$[\text{MnOH}^+] + [\text{MnSO}_4] -$$

$$\text{CV} / (\text{Vo} + \text{V}) = 0 \quad (21a)$$

$$[\text{HSO}_4^-] + [\text{SO}_4^{2-}] + [\text{FeSO}_4] + [\text{FeSO}_4] + 2[\text{Fe}(\text{SO}_4)_2] +$$

$$+ [\text{MnSO}_4] -$$

$$(\text{Co} + \text{Co}_1)\text{Vo} / (\text{Vo} + \text{V}) = 0 \quad (22a)$$

$$[\text{Fe}^{2+}] + [\text{FeOH}^+] + [\text{FeSO}_4] + [\text{Fe}^{3+}] + [\text{FeOH}^{2+}] +$$

$$[\text{Fe}(\text{OH})_2] + 2[\text{Fe}_2(\text{OH})_2] +$$

$$[\text{FeSO}_4] + [\text{Fe}(\text{SO}_4)_2] - \text{CoVo} / (\text{Vo} + \text{V}) = 0 \quad (23a)$$

The equality (not equation!)

$$[\text{K}^+] = \text{CV} / (\text{Vo} + \text{V}) \quad (20a)$$

can enter immediately Eq. 18a like a number, at defined V-value.

The set of interrelations for equilibrium constants

Concentrations of the species involved in the set of 6 equations: 33, 18a, 19a, 21a, 22a, 23a, are compatible with the complete set of equilibrium constants, specified as follows:

$$[\text{H}^+][\text{OH}^-] = 10^{-14.0}; [\text{HSO}_4^-] = 101.8[\text{H}^+][\text{SO}_4^{2-}];$$

$$[\text{H}_2\text{CO}_3] = 1016.4[\text{H}^+]^2[\text{CO}_3^{2-}];$$

$$[\text{HCO}_3^-] = 1010.1[\text{H}^+][\text{CO}_3^{2-}]; [\text{Fe}^{3+}] = [\text{Fe}^{2+}] \cdot 10A(E - 0.771);$$

$$[\text{FeOH}^+] = 104.5[\text{Fe}^{2+}][\text{OH}^-];$$

$$[\text{FeOH}^{2+}] = 1011.0[\text{Fe}^{3+}][\text{OH}^-]; [\text{Fe}(\text{OH})_2] = 1021.7[\text{Fe}^{3+}][\text{OH}^-]^2;$$

$$[\text{Fe}_2(\text{OH})_2] = 1021.7[\text{Fe}^{3+}]^2[\text{OH}^-]^2;$$

$$[\text{FeSO}_4] = 102.3[\text{Fe}^{2+}][\text{SO}_4^{2-}]; [\text{FeSO}_4] = 104.18[\text{Fe}^{3+}][\text{SO}_4^{2-}];$$

$$[\text{Fe}(\text{SO}_4)_2] = 107.4[\text{Fe}^{3+}][\text{SO}_4^{2-}]^2;$$

$$[\text{MnO}_4^-] = [\text{Mn}^{2+}] \cdot 105A(E - 1.507) + 8\text{pH}; [\text{MnO}_4^{2-}] =$$

$$[\text{Mn}^{2+}] \cdot 104A(E - 1.743) + 8\text{pH}; [\text{Mn}^{3+}] = [\text{Mn}^{2+}] \cdot 10A(E - 1.509);$$

$$[\text{MnOH}^{2+}] = 1014.2[\text{Mn}^{3+}][\text{OH}^-] \quad (35)$$

The electrode potentials E [V] are put in context with standard electrode potentials E_{0i}, expressed in SHE scale [40].

The set of independent variables

The number of equations is equal to the number of 6 independent variables, chosen as components of the vector:

$$\mathbf{x} = [x_1, \dots, x_6]^T = [E, \text{pH}, \text{pMn}^2, \text{pFe}^2, \text{pSO}_4, \text{pH}_2\text{CO}_3]^T$$

where E – potential [V], pH = $-\log[\text{H}^+]$, pMn² = $-\log[\text{Mn}^{2+}]$, pFe² = $-\log[\text{Fe}^{2+}]$, pSO₄ = $-\log[\text{SO}_4^{2-}]$, pH₂CO₃ = $-\log[\text{H}_2\text{CO}_3]$.

Mole fraction as the parameter of D+T system

All the variables, put in logarithmic scale, are considered as functions of volume V of the titrant T added during the titration $T \rightleftharpoons D$, $x_i = x_i(V)$. The V [mL] is considered as parameter of the D+T system. On this basis, the mole fraction values

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

are calculated at pre-assumed V₀, C, C₀ values. The (Φ) provides a kind of normalization (independence on V₀ value) in the system, and is taken as the independent variable on the abscissa of the related plots. The knowledge of the $x_i = x_i(V)$ values, allows also to calculate the concentrations $[X_i^{Z_i}]$ of the different species of the D+T system on the basis of relations (35) and present these changes as plots on the relevant speciation diagrams $\log [X_i^{Z_i}] = \Theta_i(\Phi)$, together with $E = E(\Phi)$ and $\text{pH} = \text{pH}(\Phi)$ relationships. Graphical presentation of the data provides an excellent tool for qualitative and quantitative evaluation of processes, occurring at any point of the titration.

All these data for the D+T system are obtained on the basis of calculations realized with use of the MATLAB [1] computer program.

Computer program

```

function F = Function_MnO4_Fe(x)

global V Vmin Vstep Vmax Vo C C1 Co C01 Co2 H OH fi pH E

global Kw pKw A K logK

global HSO4 SO4 logHSO4 logSO4

global H2CO3 HCO3 CO3

global logH2CO3 logHCO3 logCO3

global Mn7O4 Mn6O4 Mn3 Mn3OH

global logMn7O4 logMn6O4 logMn3 logMn3OH

global Mn2 Mn2OH Mn2SO4

global logMn2 logMn2OH logMn2SO4

global Fe2 Fe2OH Fe2SO4

global logFe2 logFe2OH logFe2SO4

global Fe3 Fe3OH Fe3OH2 Fe32OH2 Fe3SO4 Fe3SO42

global logFe3 logFe3OH logFe3OH2 logFe32OH2 logFe3SO4
logFe3SO42

E=x(1);

pH=x(2);

Mn2=10.^-x(3);

Fe2=10.^-x(4);

SO4=10.^-x(5);

H2CO3=10.^-x(6);

H=10.^-pH;

pKw=14;

Kw=10.^-14;

OH=Kw./H;

A=16.9;

Mn7O4=Mn2.*10.^(5.*A.*(E-1.507)+8.*pH);

Mn6O4=Mn2.*10.^(4.*A.*(E-1.743)+8.*pH);

Mn3=Mn2.*10.^(A.*(E-1.509));

Fe3=Fe2.*10.^(A.*(E-0.771));

HSO4=10.^1.8.*H.*SO4;

CO3=10.^-16.4.*H^2.*H2CO3;

HCO3=10.^10.1.*H.*CO3;

Fe2OH=10.^4.5.*Fe2.*OH;

```

```

Fe2SO4=10.^2.3.*Fe2.*SO4;

Fe3OH=10.^11.0.*Fe3.*OH;

Fe3OH2=10.^21.7.*Fe3.*OH.^2;

Fe32OH2=10.^25.1.*Fe3.^2.*OH.^2;

Fe3SO4=10.^4.18.*Fe3.*SO4;

Fe3SO42=10.^7.4.*Fe3.*SO4.^2;

Mn2OH=10.^3.4.*Mn2.*OH;

Mn2SO4=10.^2.28.*Mn2.*SO4;

Mn3OH=10.^14.2.*Mn3.*OH;

K=C.*V./(Vo+V);

%Charge balance

F=[(H-OH-HSO4-2.*SO4-HCO3-2.*CO3-+2.*Fe2+Fe2OH...
+3.*Fe3+2.*Fe3OH+Fe3OH2+4.*Fe32OH2+Fe3SO4-
Fe3SO42...
+K-Mn7O4-2.*Mn6O4+3*Mn3+2.*Mn3OH+2.*Mn2+Mn2
OH);

%Concentration balance of Mn

(Mn7O4+Mn6O4+Mn3+Mn3OH+Mn2+Mn2OH+Mn2SO4-
C.*V./(Vo+V));

%Concentration balance of Fe

(Fe2+Fe2OH+Fe2SO4+Fe3+Fe3OH+Fe3OH2+2.*Fe32OH2...
+Fe3SO4+Fe3SO42-Co.*Vo./(Vo+V));

%Concentration balance of SO4

(HSO4+SO4+Mn2SO4+Fe2SO4+Fe3SO4+2.*Fe3SO42-
(Co+Ca).*Vo./(Vo+V));

%Concentration balance of CO3

(H2CO3+HCO3+CO3-(Co2.*Vo+C1.*V))/(Vo+V));

%Electron balance

(Fe2+Fe2OH+Fe2SO4-(5.*Mn7O4+4.*Mn6O4+
Mn3+Mn3OH)...
-(Co.*Vo.-5.*C.*V.)/(Vo+V));

logMn2=log10(Mn2);

logMn2OH=log10(Mn2OH);

logMn2SO4=log10(Mn2SO4);

logMn3=log10(Mn3);

logMn3OH=log10(Mn3OH);

logMn6O4=log10(Mn6O4);

```


$$\begin{aligned} \log \text{Mn7O4} &= \log_{10}(\text{Mn7O4}); \\ \log \text{Fe2} &= \log_{10}(\text{Fe2}); \\ \log \text{Fe2OH} &= \log_{10}(\text{Fe2OH}); \\ \log \text{Fe2SO4} &= \log_{10}(\text{Fe2SO4}); \\ \log \text{Fe3} &= \log_{10}(\text{Fe3}); \\ \log \text{Fe3OH} &= \log_{10}(\text{Fe3OH}); \\ \log \text{Fe3OH2} &= \log_{10}(\text{Fe3OH2}); \\ \log \text{Fe32OH2} &= \log_{10}(\text{Fe32OH2}); \\ \log \text{Fe3SO4} &= \log_{10}(\text{Fe3SO4}); \\ \log \text{Fe3SO42} &= \log_{10}(\text{Fe3SO42}); \\ \log \text{HSO4} &= \log_{10}(\text{HSO4}); \\ \log \text{SO4} &= \log_{10}(\text{SO4}); \\ \log \text{H2CO3} &= \log_{10}(\text{H2CO3}); \\ \log \text{HCO3} &= \log_{10}(\text{HCO3}); \\ \log \text{CO3} &= \log_{10}(\text{CO3}); \\ \log K &= \log_{10}(K); \end{aligned}$$

Graphical presentation of results and discussion

The results of calculations made at $V_0=100$, $C_0=0.01$, $C=0.02$, $C_{01}=0.5$, $C_{02}=C_1 = 0$ are plotted in Figures 1,2. The jump of E on the curve in Figure 1a occurs at $\Phi = \Phi_{eq} = 0.2$, i.e., at the equivalent (eq) point where $C \cdot V_{eq} = 0.2 \cdot C_0 \cdot V_0$. Relatively small pH changes (Figure 1b) result from high buffer capacity of the titrand D [41-46]. From Figure 2a we see that $[\text{Fe}+3] \ll [\text{FeSO4}+1] \ll [\text{Fe}(\text{SO4})_2-1]$. Note that $\text{MnOH}+2$ and $\text{Mn}+3$ (not MnO_4-1) ions are the predominating manganese species immediately after crossing the related equivalence point (Figure 2b). Some points from the vicinity of equivalence point are presented in table 1.

'Variations on a theme'

Option 1. To indicate a complexation effect of sulphate ions, introduced by the H_2SO_4 solution, we compare the plots of $E = E(\Phi)$ curves: (1) the curve from Figure 1a with one (2) obtained after omission of the sulfate complexes (FeSO_4 , FeSO_4+1 , $\text{Fe}(\text{SO}_4)_2-1$, MnSO_4) from the algorithm in section 4.5. The related plots are compared in Figure 3.

Option 2. The sulphate complexes formed by $\text{Mn}+3$ ions are unknown in literature, although on the basis of analogy with other trivalent ions (e.g., $\text{Fe}+3$, $\text{Al}+3$) it could be expected that the stability constants K_i for virtual $\text{Mn}(\text{SO}_4)_i+3-2i$ complexes, $[\text{Mn}(\text{SO}_4)_i+3-2i] = K_i \cdot [\text{Mn}+3][\text{SO}_4-2]_i$, may have significant values. However, a numerical analysis of the data obtained for the pre-assumed stability constants K_i of sulphate complexes (Figure 4) with the curve obtained experimentally [14] has revealed that the $\text{Mn}(\text{SO}_4)_i+3-2i$ complexes – if they exist – are relatively weak [6].

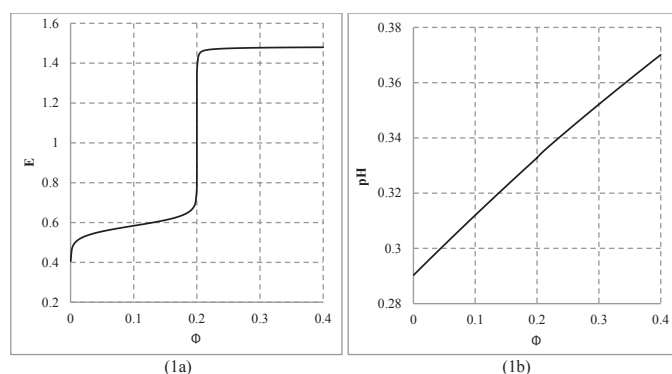


Figure 1: The relationships: (1a) $E = E(\Phi)$ and (1b) $\text{pH} = \text{pH}(\Phi)$ plotted at $(V_0, C_0, C_{01}, C) = (100, 0.01, 0.5, 0.02)$ and $C_1 = C_{02} = 0$.

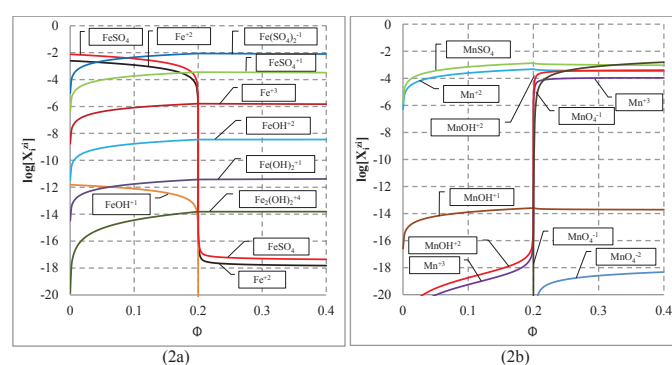


Figure 2: System II-3: The speciation curves for (2a) Mn species and (2b) Fe species plotted at $(V_0, C_0, C_{01}, C) = (100, 0.01, 0.5, 0.02)$ and $C_1 = C_{02} = 0$.

Table 1: The selected pairs (Φ, E) taken from the vicinity of $\Phi_{eq} = 0.2$ at $(V_0, C_0, C_{01}, C) = (100, 0.01, 0.5, 0.02)$ and $C_1 = C_{02} = 0$.

| Φ | E, mV |
|---------|-------|
| 0.19800 | 0.701 |
| 0.19900 | 0.719 |
| 0.19980 | 0.761 |
| 0.19990 | 0.778 |
| 0.19998 | 0.820 |
| 0.20000 | 1.034 |
| 0.20002 | 1.323 |
| 0.20010 | 1.365 |
| 0.20020 | 1.382 |
| 0.20200 | 1.442 |

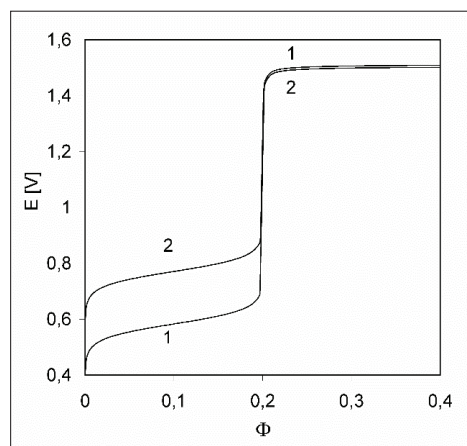


Figure 3: The $E = E(\Phi)$ relationships: 1 – as in Fig. 1a; 2 – after omission of sulphate Fe- and Mn- complexes in the related balances; $C_0 = 0.01$, $C_{01} = 0.5$, $C = 0.02$.

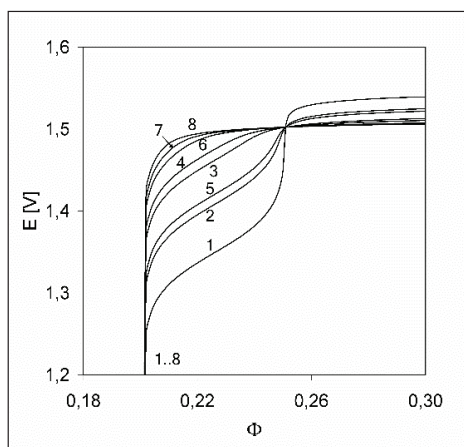


Figure 4: Fragments of hypothetical titration curves plotted for different pairs of stability constants (K_1, K_2) of the sulfate complexes $Mn(SO_4)_{j+3-2i}$: 1 – (104, 107), 2 – (103, 106), 3 – (102.5, 105), 4 – (102, 104), 5 – (104, 0), 6 – (103, 0), 7 – (102, 0), 8 – (0, 0), plotted at $C_0 = 0.01$, $C_{O1} = 0.5$, $C = 0.02$.

Final Comments

The quantitative, algebraic description of any electrolytic system according to GATES principles is based on electroneutrality rule, and on rules of conservation of particular elements in the systems, where none radioactive transformations occur [2]. The electroneutrality rule is expressed by charge balance ($f_0 = ChB$). The conservation of particular elements is expressed in terms of elemental and core balances $f_k = f(Y_k)$, where Y_k ($k=1,2,\dots,K$) is an element or core. For ordering purposes it is assumed that $Y_1 = H$, $Y_2 = O$, and the linear combination $f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(O) - f(H)$ is formulated. In redox systems, K^* electron-non-active elements/cores ('fans'), and $K - K^*$ electron-active elements ('players') are distinguished. In all examples presented here, H and O did not participated in redox systems as players. The set of K balances ($f_0, f_{12}, f_3, \dots, f_K$) is needed for mathematical formulation of a redox system (i.e., at $K^* < K$), whereas the $K-1$ balances f_0, f_3, \dots, f_K are needed for resolution of a non-redox system, where $K^* = K$ and f_{12} is the balance linearly dependent on f_0, f_3, \dots, f_K . The linear independency or dependency of f_{12} within the balances $f_0, f_{12}, f_3, \dots, f_K$ is then the general, dichotomous criterion distinguishing between redox and non-redox systems. The linear combination $\sum_{k=3}^{K^*} d_k \cdot f_k - f_0$ (Eq. 3) applied to a non-redox system (10) gives the identity, $0 = 0$, for a non-redox system, or (20) does not give the identity for a redox system, also after any linear combination with $K - K^*$ balances for the players in this system. These regularities are valid for coefficients d_k equal to oxidation numbers (ONs) of the elements in the corresponding balances $f_k = f(Y_k)$ for elements/cores Y_k related to fans.

The f_{12} and any linear combination of f_{12} with f_0, f_3, \dots, f_K , have full properties of Generalized Electron Balance (GEB), completing the set of K balances, $f_0, f_{12}, f_3, \dots, f_K$, needed for resolution of a redox system, of any degree of complexity. The supreme role of this independency/dependency criterion, put also in context with calculation of ONs, is of great importance,

in context with the contractual nature of the ON concept known from the literature issued hitherto [47-49]. These regularities are the clear confirmation of the Emmy Noether's general theorem [50], applied to conservation laws of a physical/electrolytic system, expressed in terms of algebraic equations, where GEB is perceived as the Law of Nature [15], as the hidden connection of physicochemical laws, and as the breakthrough in thermodynamic theory of electrolytic redox systems. Resolution of several redox systems, according to principles of Generalized Approach to Electrolytic Systems (GATES), is presented. The GATES/GEB is the best thermodynamic approach of electrolytic redox systems, of any degree of complexity. The Generalized Equivalent Mass (GEM) concept [14], fully compatible with the GATES principles, was introduced. The mathematical models, applicable for handling the results obtained from potentiometric titrations in redox systems, were also presented. The chapter offers – undoubtedly – the best possible ways to resolution of the issues raised. Formulation of an electrolytic redox system specified in section 3.1.3 illustrates the huge possibilities/advantages inherent in GATES/GEB.

All the regularities specified above are valid for redox and non-redox systems of any degree of complexity, also for the multi-solvent systems [51-54].

The key role of H and O (not free electrons, e^-) in redox systems, inherent in f_{12} , was stressed in [23]. Contrary to appearances, established by the current paradigm "obligatory" till now, the criterion distinguishing non-redox and redox systems is not immediately associated with free electrons in the system. The new/fundamental/practical criterion involved with $f_{12} = 2 \cdot f(O) - f(H)$ and its properties, unknown in earlier literature, provides a kind of uniformity in the formulas derived for this purpose. This fact, especially the simple calculations of free electron concentrations in redox systems [23], deny the unique role of free electrons in redox reactions. On the other hand, it points to the decisive role of H and O in redox systems [2], suggested elsewhere, in earlier theoretical/hypothetical considerations on these systems. Here is the hidden simplicity, which had to be discovered, as the Approach II to GEB. The author TM contends that the discovery of the Approach II GEB would most likely be impossible without the prior discovery of the Approach I to GEB. The GEB concept, valid for electrolytic redox systems, is the emanation of balances for H and O, referred to aqueous media. GEB is compatible with other (charge and concentration) balances and enables to resolve the electrolytic (mono- or/and two-phase) redox systems of any degree of complexity, within the scope of GATES, perceived as the thermodynamic approach to equilibrium and metastable systems, where all necessary physicochemical knowledge on the systems tested is involved. The GATES is perceived as the unrivalled tool applicable, among others: (a) to mathematical modelling of thermodynamic behavior of the systems, (b) in choice of optimal a priori conditions of chemical analyses, and (c) in gaining chemical information invisible in real experiments, in general.

GATES/GEB is a counter-proposal in relation to earlier IUPAC decisions, presented in three subsequent editions of the Orange Book, and based on the reaction stoichiometry;

that viewpoint was criticized unequivocally/exhaustively/convincingly, especially in a series of authors' articles cited herein. It were demonstrated, on examples of redox systems of different complexity, that stoichiometry is a secondary/derivative/"fragile" concept, from the viewpoint of GATES, and GATES/ GEB, in particular.

Conservation laws of physics are very closely related to the symmetry of physical laws under various transformations. The nature of these connections is an intriguing physical problem. The theory of these connections, as it appears in classical physics, constitutes one of the most beautiful aspects of mathematical physics. It confirms a general theorem of Emmy Noether which states that symmetries and conservation laws of a physical system correspond to each other [50]. The Noether's conceptual approach to algebra led to a body of principles unifying algebra, geometry, linear algebra, topology, and logic. The theory of this connection constitutes one of the most beautiful chapters of mathematical physics.

Concluding, GATES is the overall, thermodynamic approach to redox and non-redox, static and dynamic, single and multiphase equilibrium, metastable and non-equilibrium electrolytic systems, of any degree of complexity. Possibilities of GATES/GEB are far greater than ones offered by the actual physicochemical knowledge related to the system in question.

Stoichiometry, oxidation number, equivalent mass, order of reaction, equivalent mass [14], etc. are derivative (not primary!) concepts within GATES. The Equilibrium Law (EL), based on the Gibbs function and the Lagrange multipliers idea [15], can be put instead of Mass Action Law (MAL), based on a stoichiometric reaction notation, and other principles. Equilibrium, kinetic and metastable systems are distinguished. Within GATES, thermodynamics of electrolytic systems is based on purely algebraic principles; the stoichiometry is considered here only as a kind of "dummy" [22,23,55].

Summarizing, this paper offers the best possible ways to resolution of the issues raised.

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