

New Paradigm in Thermodynamic Formulation of Dynamic Redox Systems

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Abstract: The Generalized Approach to Electrolytic Systems (GATES/GEB) is the recommended paradigm applicable to thermodynamic formulation of electrolytic redox systems of any degree of complexity where Generalized Electron Balance (GEB) completes the set of equations needed for quantitative description of the redox system tested. Two equivalent Approaches (I, II) to GEB are formulated herein for the potentiometric titration in the (FeSO₄ + H₂C₂O₄ + H₂SO₄, KMnO₄) system (D+T system) and in related subsystems, (D₁+T) and (D₂+T), taken as formal examples. Among others, the general criterion distinguishing between redox and non-redox systems is indicated. Further regularities related to these systems are clearly reported.

Keywords: Thermodynamics of electrolytic redox systems; GATES/GEB; Potentiometric titration; Simulation of dynamic redox systems

1. Introduction

Thermodynamic formulation of an electrolytic system (aqueous solution) is based on fundamental laws of the matter conservation. These laws are expressed, in algebraic form, as the complete set of independent relations, composed of charge and elemental/core balances and interrelations for the corresponding equilibrium constants, where some species of the system are involved. These balances interrelated components of the system and the species formed in this system. A core is considered here as a cluster of different atoms with defined composition (expressed by its chemical formula), structure and external charge, unchanged in the system in question. For example, SO₄⁻² is a core within different sulphate components: FeSO₄·xH₂O, H₂SO₄ and hydrated species: HSO₄⁻¹, SO₄⁻², FeSO₄⁺, FeSO₄⁺¹, Fe(SO₄)₂⁻¹, MnSO₄ in the D₁+T system considered herein. The charge balance expresses the electroneutrality of the system, whereas the elemental/core balances, interrelating components of the system and the species in the system thus formed, express the conservation of all elements in the system. It is also assumed that only non-radioactive elements are involved in the considered system, where all basic types (acid-base, complexation, precipitation and redox) of chemical reactions run parallelly and/or sequentially.

Redox and non-redox electrolytic systems, of different complexity, were formulated by Michałowski (1992) according to

Generalized Approach to Redox Systems (GATES) principles. When related to redox systems, the acronym GATES/GEB GATES is applied. Electrolytic redox systems of different complexity, formulated according to GATES/GEB principles, were presented.^[1-56] The key role in redox systems plays Generalized Electron Balance (GEB), considered as the Law of Nature^[32,39,56] discovered (1992, 2005) by Michałowski, and formulated as the Approaches (I,II) to GEB.

The Approach I to GEB (1992) is based on a “card game” principle, with electron active elements as “players”, electron non-active elements as “fans”, and electrons as “money”.^[32,39,56] The transmission of electrons/money occurs between the players and does not occur between fans (the fans accounts are intact).

From the Approach II to GEB (2005) viewpoint, the fundamental property of electrolytic systems is involved with 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 dependence/independence of f_{12} on the set f_0, f_3, \dots, f_k composed of charge balance ($f_0 = \text{ChB}$) and other elemental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) is the general criterion distinguishing between non-redox and redox systems.

For modelling purposes, an electrolytic system is perceived as a macroscopic part of the Universe, which is selected for consideration. Furthermore, according to GATES principles, we also assume it as *a priori* closed system/subsystems “matter \rightleftharpoons system/subsystems \rightleftharpoons heat” separated from its environment by diathermal (e.g. freely permeable by heat) walls as boundaries, preventing (\rightleftharpoons) the matter (e.g. H₂O, CO₂, O₂,...) exchange but

allowing (\Leftrightarrow) exchange of heat, resulting from exo- or endothermic processes occurring in a given system. In other words, as any process represented by titration, this approach assumes to be performed in quasistatic manner, under isothermal conditions. Constant temperature is one of the conditions securing constancy of equilibrium constants related to the system in question.

Herein aqueous media are investigated, in which species $X_i^{z_i}$ are considered in their natural/factual forms, i.e., as hydrates $X_i^{z_i} \cdot n_{iw}$, where z_i is a charge of this species ($z_i = 0, \pm 1, \pm 2, \dots$) expressed in terms of elementary charge unit, $e = F/N_A$ (F – Faraday’s constant, N_A – Avogadro’s number); n_{iw} (≥ 0) is the mean number of water ($W=H_2O$) molecules attached to $X_i^{z_i}$. For these species in aqueous medium, we apply the notation $X_i^{z_i}(N_i, n_i)$, where N_i is a number of entities of these species in the system, and $n_i = n_{iw} = n_i H_2O$.

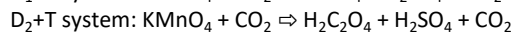
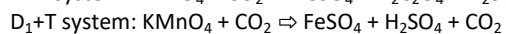
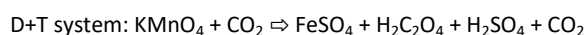
Let us assume the electrolytic system formed from $N_{0j}(j=1, \dots, J)$ molecules of j -th kind, as components of the system, with non-radioactive elements involved. The mixture thus obtained involves N_i ($i=1, \dots, I$) species of i -th kind.

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

- 1) the law of charge conservation, expressed by charge balance ($f_0 = ChB$); the f_0 expresses electroneutrality (zero net charge) of the electrolytic (sub)system, and interrelates the numbers N_i of a subset of charged species (ions of i -th kind, $z_i \neq 0$) in the (sub)system;
- 2) the law of conservation of particular elements/cores Y_k ($k=1, \dots, K$), expressing elemental/core balances $f_k = f(Y_k)$, where the numbers N_{0j} of components and the numbers N_i of the species formed in the system are interrelated.

Static and dynamic systems are distinguished. A static system is obtained after a disposable mixing specific chemical compounds as solutes, and water as solvent. A dynamic system can be realized according to titrimetric mode, where – at defined point of the titration – V mL of titrant T is added, in successive portions, into V_0 mL of titrand D , and V_0+V mL of the $D+T$ mixture is thus obtained at this point of the titration; if the volumes V_0 and V are additive. The D and T are subsystems of the $D+T$ system.

In this work, we consider three titrand + titrant systems, denoted as: $D+T$, D_1+T and D_2+T , which are specified as follows:



The $D+T$ is more complex than D_1+T and D_2+T .

2. The balances and their linear combinations

For a beginning, let us consider a set of $K+1$ linear, algebraic equations:

$$\sum_{i=1}^I a_{ki} \cdot X_i = b_k \Leftrightarrow \sum_{i=1}^I a_{ki} \cdot X_i - b_k = 0 \quad (k=0, \dots, K) \quad (1)$$

where a_{ki} are the coefficients and b_k – free terms. When multiplying Eq. 1 by β_k , after subsequent summation we have

$$\sum_{k=0}^K \beta_k \cdot \sum_{i=1}^I a_{ki} \cdot X_i = \sum_{k=0}^K \beta_k \cdot b_k \Leftrightarrow \sum_{i=1}^I X_i \cdot \sum_{k=0}^K \beta_k \cdot a_{ki} = \sum_{k=0}^K \beta_k \cdot b_k \quad (2)$$

Assuming

$$b_k = \sum_{j=1}^J \beta_{kj} \cdot X_{0j} \quad (3)$$

By combining Eqs. 2 and 3, we have

$$\sum_{i=1}^I X_i \cdot \sum_{k=0}^K \beta_k \cdot a_{ki} = \sum_{j=1}^J X_{0j} \cdot \sum_{k=0}^K \beta_k \cdot b_{kj} \quad (4)$$

Referring to the problem in question, we assume: $X_i = N_i$, $X_{0j} = N_{0j}$ in Eq. 4, and we write

$$\sum_{i=1}^I N_i \cdot \sum_{k=0}^K \beta_k \cdot a_{ki} = \sum_{j=1}^J N_{0j} \cdot \sum_{k=0}^K \beta_k \cdot b_{kj} \quad (5)$$

The charge balance, $f_0 = ChB$, is expressed as follows

$$f_0 = \sum_{i=1}^I a_{0i} \cdot N_i = \sum_{i=2}^I Z_i \cdot N_i = 0 \quad (6)$$

Where $a_{0i} = z_i$; $z_1 = 0$ for $x_1^{z_1} = H_2O$, $z_2 = 1$ for $x_2^{z_2} = H^{+1}$, $z_3 = -1$ for $x_3^{z_3} = OH^{-1}$, ...

The elemental/core balances $f_1 = f(H)$, $f_2 = f(O)$ and $f_k = f(Y_k)$ ($Y_k \neq H, O, k \geq 3, \dots, K$) are written as follows:

$$\begin{aligned} f_1 = f(H) &= \sum_{i=1}^I (a_{1i} + 2n_{iw}) \cdot N_i - \sum_{j=1}^J b_{1j} \cdot N_{0j} = 0 \text{ for } Y_1 = H, \\ f_2 = f(O) &= \sum_{i=1}^I (a_{2i} + n_{iw}) \cdot N_i - \sum_{j=1}^J b_{2j} \cdot N_{0j} = 0 \text{ for } Y_2 = O \\ f_k &= \sum_{i=1}^I a_{ki} \cdot N_i - \sum_{j=1}^J b_{kj} \cdot N_{0j} = 0, \dots \\ f_K &= \sum_{i=1}^I a_{Ki} \cdot N_i - \sum_{j=1}^J b_{Kj} \cdot N_{0j} = 0 \end{aligned}$$

where a_{ki} and b_{kj} are the numbers of atoms/cores of k -th element/core in i -th species and j -th component, respectively. Then the balance

$$f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(O) - f(H) = \sum_{i=2}^I (2a_{2i} - a_{1i}) \cdot N_i - \sum_{j=1}^J (2b_{2j} - b_{1j}) \cdot N_{0j} = 0 \quad (7)$$

is formulated. In the balances f_0, f_3, \dots, f_K related to aqueous media, the terms involved with water, i.e., N_{0j} (for j related to H_2O , as the component), N_1 , and all $n_i = n_{iw}$ are cancelled within f_{12} (Eq. 7).

The linear combination of all K balances: $f_0, f_{12}, f_3, \dots, f_K$ can be then presented in equivalent forms:

$$\sum_{i=1}^I N_i \cdot (z_i + \sum_{k=1}^K \beta_k \cdot a_{ki}) = \sum_{j=1}^J N_{0j} \cdot \sum_{k=1}^K \beta_k \cdot b_{kj} \quad (8a)$$

$$\begin{aligned} \sum_{i=1}^I N_i \cdot z_i + \sum_{k=1}^K \beta_k \cdot (\sum_{i=1}^I N_i \cdot a_{ki} - \sum_{j=1}^J N_{0j} \cdot b_{kj}) &= 0 \\ f_0 + f_{12} + \sum_{k=3}^K \beta_k \cdot f_k &= 0 \\ f_0 + 2 \cdot f_2 - f_1 + \sum_{k=3}^K \beta_k \cdot f_k &= 0 \\ d_1 \cdot f(H) + d_2 \cdot f(O) + \sum_{k=3}^K d_k \cdot f(Y_k) - f_0 &= 0 \end{aligned} \quad (8b)$$

where $d_1 = +1$, $d_2 = -2$, $d_k = (k = 3, \dots, K)$ are defined as oxidation numbers of atoms in elemental balances, or resultant (sum) value of ONs calculated for each element in a core for a given component and species.^[51]

If all multipliers at N_i and N_{0j} are cancelled simultaneously, from Eq. 8a we have:

$$z_i + \sum_{k=1}^K d_k \cdot a_{ki} = 0 \text{ and } \sum_{k=1}^K d_k \cdot b_{kj} = 0$$

for all i and j values ($i = 1, \dots, I$; $j = 1, \dots, J$), i.e., Eq. 8a is transformed into identity

$$\sum_{i=1}^I N_i \cdot 0 = \sum_{j=1}^J N_{0j} \cdot 0 \Leftrightarrow 0 = 0 \quad (9)$$

The transformation of a set of the equations $f_0, f_{12}, f_3, \dots, f_K$ into the identity, $0 = 0$, proves the linear dependence between these balances in the system considered.

Formulation of the proper linear combination, with $d_k (k=1, \dots, K)$ equal to the related oxidation number (ON) values, is then applicable to check the linear dependency or independency of the balances. It is very effective/simplest way of checking/stating the linear dependence of the K balances: $f_0, f_{12}, f_3, \dots, f_K$ related to non-redox systems, named as the transformation of the linear combination of $f_0, f_1, f_2, f_3, \dots, f_K$ to the identity, $0 = 0$. It is the simplest form of the linear combination of $f_0, f_1, f_2, f_3, \dots, f_K$ for a non-redox system. For a redox system, the proper linear combination of $f_0, f_1, f_2, f_3, \dots, f_K$ with d_k equal to the related oxidation numbers (ONs), is the way towards the simplest/shortest form of GEB, different from the identity, $0 = 0$.

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

$$f_k = \sum_{i=1}^I a_{ki} \cdot N_i - \sum_{j=1}^J b_{kj} \cdot N_{0j} = 0 \Leftrightarrow \sum_{i=1}^I a_{ki} \cdot N_i = \sum_{j=1}^J b_{kj} \cdot N_{0j} \quad (10)$$

for elements with negative oxidation numbers, or

$$-f_k = \sum_{j=1}^J b_{kj} \cdot N_{0j} - \sum_{i=1}^I a_{ki} \cdot N_i = 0 \Leftrightarrow \sum_{j=1}^J b_{kj} \cdot N_{0j} = \sum_{i=1}^I a_{ki} \cdot N_i \quad (11)$$

for elements with positive oxidation numbers, $k \in 3, \dots, K$.

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.

2.1. Components and species in the (sub) systems tested

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 $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ (N_{04}) + $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (N_{05}) + H_2SO_4 (N_{06}) + CO_2 (N_{07}) + H_2O (N_{08}) in V_0 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), Fe^{+2} (N_7, n_7), FeOH^{+1} (N_8, n_8), FeSO_4 (N_9, n_9), Fe^{+3} (N_{10}, n_{10}), FeOH^{+2} (N_{11}, n_{11}), $\text{Fe}(\text{OH})_2^{+1}$ (N_{12}, n_{12}), $\text{Fe}_2(\text{OH})_2^{+4}$ (N_{13}, n_{13}), FeSO_4^{+1} (N_{14}, n_{14}), $\text{Fe}(\text{SO}_4)_2^{-1}$ (N_{15}, n_{15}), $\text{H}_2\text{C}_2\text{O}_4$ (N_{16}, n_{16}), $\text{HC}_2\text{O}_4^{-1}$ (N_{17}, n_{17}), $\text{C}_2\text{O}_4^{-2}$ (N_{18}, n_{18}), H_2CO_3 (N_{19}, n_{19}), HCO_3^{-1} (N_{20}, n_{20}), CO_3^{-2} (N_{21}, n_{21}), MnO_4^{-1} (N_{22}, n_{22}), MnO_4^{-2} (N_{23}, n_{23}), Mn^{+3} (N_{24}, n_{24}), MnOH^{+2} (N_{25}, n_{25}),

Mn^{+2} (N_{26}, n_{26}), MnOH^{+1} (N_{27}, n_{27}), MnSO_4 (N_{28}, n_{28}), $\text{Fe}(\text{C}_2\text{O}_4)_2^{-2}$ (N_{29}, n_{29}), $\text{Fe}(\text{C}_2\text{O}_4)_3^{-4}$ (N_{30}, n_{30}), $\text{FeC}_2\text{O}_4^{+1}$ (N_{31}, n_{31}), $\text{Fe}(\text{C}_2\text{O}_4)_2^{-1}$ (N_{32}, n_{32}), $\text{Fe}(\text{C}_2\text{O}_4)_3^{-3}$ (N_{33}, n_{33}), MnC_2O_4 (N_{34}, n_{34}), $\text{Mn}(\text{C}_2\text{O}_4)_2^{-2}$ (N_{35}, n_{35}), $\text{Mn}(\text{C}_2\text{O}_4)_3^{-4}$ (N_{36}, n_{36}), $\text{MnC}_2\text{O}_4^{+1}$ (N_{37}, n_{37}), $\text{Mn}(\text{C}_2\text{O}_4)_2^{-1}$ (N_{38}, n_{38}), $\text{Mn}(\text{C}_2\text{O}_4)_3^{-3}$ (N_{39}, n_{39}), FeC_2O_4 ($a_1 \cdot N_{40}, n_{40}$), MnC_2O_4 ($a_2 \cdot N_{41}, n_{41}$), MnSO_4^{+1} ($b \cdot N_{42}, n_{42}$), $\text{Mn}(\text{SO}_4)_2^{-1}$ ($b \cdot N_{43}, n_{43}$). (12)

The notation/numbering applied in (12) for D+T is also obligatory for D, D_1 , D_2 , T, D_1+T and D_2+T .

A few comments

- Three electron-active elements: Fe, C, and Mn, termed as players, are involved in this D+T system; Mn as KMnO_4 , Fe as $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$, C as $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and CO_2 participate in the transfer of electrons. CO_2 is one of the products of the oxalate oxidation, and also the admixture from air, introduced – as a rule – in laboratory water, being in contact with CO_2 from air, on the step of the D, D_1 , D_2 and T preparation.
- The multiplier $a_1 = 1$ if FeC_2O_4 is the equilibrium solid phase in the system; otherwise, $a_1 = 0$;
- The multiplier $a_2 = 1$ if MnC_2O_4 is the equilibrium solid phase in the system; otherwise, $a_2 = 0$;
- The complexes MnSO_4^{+1} and $\text{Mn}(\text{SO}_4)_2^{-1}$ and their stability constants are unknown in literature, although their existence is suggested by analogous complexes formed e.g. by Fe^{+3} ions; so we put $b = 1$ if they are pre-assumed in the model applied; otherwise $b = 0$;
- Precipitation of MnO_2 and other solid phases, e.g. $\text{Fe}(\text{OH})_3$, is not possible at low pH, and then at high buffer capacity of D+T, D_1+T or D_2+T , resulting from presence of H_2SO_4 .

On the step of arranging the appropriate balances, we assume that:

- all the species in (12) are included in condensed (solution or solution + precipitate) phases, i.e. the (arbitrary) assumption of the closed system is valid, on the step of D and T preparations, and on the step of the titration in the case of the D+T system;
- all CO_2 molecules, i.e., these resulting from oxidation of oxalate species and those from CO_2 admixture in water used for preparation of D and T, form the hydrated $\text{H}_2\text{CO}_3^{-2+i}$ ($i=0,1,2$) species;
- all equilibrium constants are valid at each stage of the titration in the D+T system. In laboratory practice, the titration is performed in an open system, at non-isothermal conditions.

Oxidation of oxalate into carbonate species in the D+T and D_2+T system requires preliminary warming (50-60°C) the titrand. At such conditions of analysis, equilibrium constants are different from those (close to 20°C) at which the values of these constants were obtained and collected in the related tables.^[6] Moreover, during the titration, temperature of D+T or D_2+T system is not kept constant. When the temperature changes, the density of the solution will also change; i.e., concentrations of the solutes are changing too.

3. The D+T system

3.1. Approach I to GEB for the D+T system

One atom of Mn has $Z_{Mn}=25$ manganese electrons, one atom of Fe has $Z_{Fe}=26$ iron electrons, one atom of C has $Z_C=6$ carbon electrons. Therefore, N_{05} molecules of $FeSO_4 \cdot xH_2O$ involve $(Z_{Fe}-2)N_{04}$ of Fe-electrons, $N_{02}+N_{07}$ molecules of CO_2 involve $(Z_C-4)(N_{02}+N_{07})$ of C-electrons, N_{05} molecules of $H_2C_2O_4 \cdot 2H_2O$ involve $2(Z_C-3)N_{05}$ of C-electrons, and N_{01} molecules of $KMnO_4$ involve $(Z_{Mn}-7) \cdot N_{01}$ of Mn-electrons. Thus, the total number of Fe, C and Mn electrons introduced by these components is $(Z_{Fe}-2)N_{04} + (Z_C-4)(N_{02}+N_{07}) + 2(Z_C-3)N_{05} + (Z_{Mn}-7)N_{01}$. After mixing, the components of the D and T subsystems forming the D+T system, and electrons of the players introduced by these components are involved in the appropriate species of the D+T system. Then we state that:

N_7 species $Fe^{+2} \cdot n_7H_2O$ involve $(Z_{Fe}-2) \cdot N_7$ of Fe electrons;
 N_8 species $FeOH^{+1} \cdot n_8H_2O$ involve $(Z_{Fe}-2) \cdot N_8$ of Fe electrons;
 N_9 species $FeSO_4 \cdot n_9H_2O$ involve $(Z_{Fe}-2) \cdot N_9$ of Fe electrons;
 N_{10} species $Fe^{+3} \cdot n_{10}H_2O$ involve $(Z_{Fe}-3) \cdot N_{10}$ of Fe electrons;
 N_{11} species $FeOH^{+2} \cdot n_{11}H_2O$ involve $(Z_{Fe}-3) \cdot N_{11}$ of Fe electrons;
 N_{12} species $Fe(OH)_2^{+2} \cdot n_{12}H_2O$ involve $(Z_{Fe}-3) \cdot N_{12}$ Fe electrons;
 N_{13} species $Fe_2(OH)_2^{+4} \cdot n_{13}H_2O$ involve $2(Z_{Fe}-3) \cdot N_{13}$ of Fe electrons;
 N_{14} species $FeSO_4^{+1} \cdot n_{14}H_2O$ involve $(Z_{Fe}-3) \cdot N_{14}$ of Fe electrons;
 N_{15} species $Fe(SO_4)_2^{-1} \cdot n_{15}H_2O$ involve $(Z_{Fe}-3) \cdot N_{15}$ of Fe electrons;
 N_{16} species $H_2C_2O_4 \cdot n_{16}H_2O$ involve $2(Z_C-3) \cdot N_{16}$ of C electrons;
 N_{17} species $HC_2O_4^{-1} \cdot n_{17}H_2O$ involve $2(Z_C-3) \cdot N_{17}$ of C electrons;
 N_{18} species $C_2O_4^{-2} \cdot n_{18}H_2O$ involve $2(Z_C-3) \cdot N_{18}$ of C electrons;
 N_{19} species $H_2CO_3 \cdot n_{19}H_2O$ involve $(Z_C-4) \cdot N_{19}$ of C electrons;
 N_{20} species $HCO_3^{-1} \cdot n_{20}H_2O$ involve $(Z_C-4) \cdot N_{20}$ of C electrons;
 N_{21} species $CO_3^{-2} \cdot n_{21}H_2O$ involve $(Z_C-4) \cdot N_{21}$ of C electrons;
 N_{22} species $MnO_4^{-1} \cdot n_{22}H_2O$ involve $(Z_{Mn}-7) \cdot N_{22}$ of Mn electrons;
 N_{23} species $MnO_4^{-2} \cdot n_{23}H_2O$ involve $(Z_{Mn}-6) \cdot N_{23}$ of Mn electrons;
 N_{24} species $Mn^{+3} \cdot n_{24}H_2O$ involve $(Z_{Mn}-3) \cdot N_{24}$ of Mn electrons;
 N_{25} species $MnOH^{+2} \cdot n_{25}H_2O$ involve $(Z_{Mn}-3) \cdot N_{25}$ of Mn electrons;
 N_{26} species $Mn^{+2} \cdot n_{26}H_2O$ involve $(Z_{Mn}-2) \cdot N_{26}$ of Mn electrons;
 N_{27} species $MnOH^{+1} \cdot n_{27}H_2O$ involve $(Z_{Mn}-2) \cdot N_{27}$ of Mn electrons;
 N_{28} species $MnSO_4 \cdot n_{28}H_2O$ involve $(Z_{Mn}-2) \cdot N_{28}$ of Mn electrons;
 N_{29} species $Fe(C_2O_4)_2^{-2} \cdot n_{29}H_2O$ involve $(Z_{Fe}-2+4(Z_C-3)) \cdot N_{29}$ of Fe+C electrons;
 N_{30} species $Fe(C_2O_4)_3^{-4} \cdot n_{30}H_2O$ involve $(Z_{Fe}-2+6(Z_C-3)) \cdot N_{30}$ of Fe+C electrons;
 N_{31} species $FeC_2O_4^{+1} \cdot n_{31}H_2O$ involve $(Z_{Fe}-3+2(Z_C-3)) \cdot N_{31}$ of Fe+C electrons;
 N_{32} species $Fe(C_2O_4)_2^{-1} \cdot n_{32}H_2O$ involve $(Z_{Fe}-3+4(Z_C-3)) \cdot N_{32}$ of Fe+C electrons;
 N_{33} species $Fe(C_2O_4)_3^{-3} \cdot n_{33}H_2O$ involve $(Z_{Fe}-3+6(Z_C-3)) \cdot N_{33}$ Fe+C electrons;
 N_{34} species $MnC_2O_4 \cdot n_{34}H_2O$ involve $(Z_{Mn}-2+2(Z_C-3)) \cdot N_{34}$ of Mn+C electrons;
 N_{35} species $Mn(C_2O_4)_2^{-2} \cdot n_{35}H_2O$ involve $(Z_{Mn}-2+4(Z_C-3)) \cdot N_{35}$ of Mn+C electrons;
 N_{36} species $Mn(C_2O_4)_3^{-4} \cdot n_{36}H_2O$ involve $(Z_{Mn}-2+6(Z_C-3)) \cdot N_{36}$ of Mn+C electrons;
 N_{37} species $MnC_2O_4^{+1} \cdot n_{37}H_2O$ involve $(Z_{Mn}-3+2(Z_C-3)) \cdot N_{37}$ of Mn+C electrons;

N_{38} species $Mn(C_2O_4)_2^{-1} \cdot n_{38}H_2O$ involve $(Z_{Mn}-3+4(Z_C-3)) \cdot N_{38}$ of Mn+C electrons;
 N_{39} species $Mn(C_2O_4)_3^{-3} \cdot n_{39}H_2O$ involve $(Z_{Mn}-3+6(Z_C-3)) \cdot N_{39}$ of Mn+C electrons;
 $a_1 \cdot N_{40}$ species $FeC_2O_4 \cdot n_{40}H_2O$ involve $a_1 \cdot (Z_{Fe}-2 + 2(Z_C-3)) \cdot N_{40}$ of Fe+C electrons;
 $a_2 \cdot N_{41}$ species $MnC_2O_4 \cdot n_{41}H_2O$ involve $a_2 \cdot (Z_{Mn}-2+2(Z_C-3)) \cdot N_{41}$ of Mn+C electrons;
 $b \cdot N_{42}$ species $MnSO_4^{+1} \cdot n_{42}H_2O$ involve $b \cdot (Z_{Mn}-3) \cdot N_{42}$ of Mn electrons;
 $b \cdot N_{43}$ species $Mn(SO_4)_2^{-1} \cdot n_{43}H_2O$ involve $b \cdot (Z_{Mn}-3) \cdot N_{43}$ of Mn electrons.

The comparison of the total numbers of Fe, C and Mn electrons in components and species gives the following equation

$$(Z_{Fe}-2)(N_7 + N_8 + N_9) + (Z_{Fe}-3) \cdot (N_{11} + N_{12} + 2N_{13} + N_{14} + N_{15}) + 2(Z_C-3) \cdot (N_{16} + N_{17} + N_{18}) + (Z_C-4) \cdot (N_{19} + N_{20} + N_{21}) + (Z_{Mn}-7) \cdot N_{22} + (Z_{Mn}-6) \cdot N_{23} + (Z_{Mn}-3) \cdot (N_{24} + N_{25}) + (Z_{Mn}-2) \cdot (N_{26} + N_{27} + N_{28}) + (Z_{Fe}-2 + 2 \cdot 2(Z_C-3)) \cdot N_{29} + (Z_{Fe}-2 + 3 \cdot 2(Z_C-3)) \cdot N_{30} + (Z_{Fe}-3+2(Z_C-3)) \cdot N_{31} + (Z_{Fe}-3 + 2 \cdot 2(Z_C-3)) \cdot N_{32} + (Z_{Fe}-3 + 3 \cdot 2(Z_C-3)) \cdot N_{33} + (Z_{Mn}-2+2(Z_C-3)) \cdot N_{34} + (Z_{Mn}-2 + 2 \cdot 2(Z_C-3)) \cdot N_{35} + (Z_{Mn}-2 + 3 \cdot 2(Z_C-3)) \cdot N_{36} + (Z_{Mn}-3+2(Z_C-3)) \cdot N_{37} + (Z_{Mn}-3 + 2 \cdot 2(Z_C-3)) \cdot N_{38} + (Z_{Mn}-3 + 3 \cdot 2(Z_C-3)) \cdot N_{39} + a_1 \cdot (Z_{Fe}-2 + 2(Z_C-3)) \cdot N_{40} + a_2 \cdot (Z_{Mn}-2+2(Z_C-3)) \cdot N_{41} + b \cdot (Z_{Mn}-3) \cdot (N_{42} + N_{43}) = (Z_{Fe}-2) \cdot N_{04} + 2(Z_C-3) \cdot N_{05} + (Z_C-4) \cdot (N_{02}+N_{07}) + (Z_{Mn}-7) \cdot N_{01} \quad (13)$$

defined as the GEB for the D+T system formulated according to Approach I to GEB.

3.2. Formulation of the D+T system according to Approach II to GEB

On the basis of the list (12) of the species we have the balances:

$$f_0 = \text{ChB}$$

$$N_2 - N_3 + N_4 - N_5 - 2N_6 + 2N_7 + N_8 + 3N_{10} + 2N_{11} + N_{12} + 4N_{13} + N_{14} - N_{15} - N_{17} - 2N_{18} - N_{20} - 2N_{21} - N_{22} - 2N_{23} + 3N_{24} + 2N_{25} + 2N_{26} + N_{27} - 2N_{29} - 4N_{30} + N_{31} - N_{32} - 3N_{33} - 2N_{35} - 4N_{36} + N_{37} - N_{38} - 3N_{39} + b \cdot N_{42} - b \cdot N_{43} = 0 \quad (14)$$

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

$$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + 2N_4n_4 + N_5(1 + 2n_5) + 2N_6n_6 + 2N_7n_7 + N_8(1 + 2n_8) + 2N_9n_9 + 2N_{10}n_{10} + N_{11}(1 + 2n_{11}) + N_{12}(2 + 2n_{12}) + N_{13}(2 + 2n_{13}) + 2N_{14}n_{14} + 2N_{15}n_{15} + N_{16}(2 + 2n_{16}) + N_{17}(1 + 2n_{17}) + 2N_{18}n_{18} + N_{19}(2 + 2n_{19}) + N_{20}(1 + 2n_{20}) + 2N_{21}n_{21} + 2N_{22}n_{22} + 2N_{23}n_{23} + 2N_{24}n_{24} + N_{25}(1 + 2n_{25}) + 2N_{26}n_{26} + N_{27}(1 + 2n_{27}) + 2N_{28}n_{28} + 2N_{29}n_{29} + 2N_{30}n_{30} + 2N_{31}n_{31} + 2N_{32}n_{32} + 2N_{33}n_{33} + 2N_{34}n_{34} + 2N_{35}n_{35} + 2N_{36}n_{36} + 2N_{37}n_{37} + 2N_{38}n_{38} + 2N_{39}n_{39} + 2a_1 \cdot N_{40}n_{40} + 2a_2 \cdot N_{41}n_{41} + 2b \cdot N_{42}n_{42} + 2b \cdot N_{43}n_{43} = 2N_{03} + 2xN_{04} + 6N_{05} + 2N_{06} + 2N_{08}$$

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

$$N_1 + N_2n_2 + N_3(1 + n_3) + N_4n_4 + N_5(4 + n_5) + N_6(4 + n_6) + N_7n_7 + N_8(1 + n_8) + N_9(4 + n_9) + N_{10}n_{10} + N_{11}(1 + n_{11}) + N_{12}(2 + n_{12}) + N_{13}(2 + n_{13}) + N_{14}(4 + n_{14}) + N_{15}(8 + n_{15}) + N_{16}(4 + n_{16}) + N_{17}(4 + n_{17}) + N_{18}(4 + n_{18}) + N_{19}(3 + n_{19}) + N_{20}(3 + n_{20}) + N_{21}(3 + n_{21}) + N_{22}(4 + n_{22}) + N_{23}(4 + n_{23}) + N_{24}n_{24} + N_{25}(1 + n_{25}) + N_{26}n_{26} + N_{27}(1 + n_{27}) + N_{28}(4 + n_{28}) + N_{29}(8 + n_{29}) + N_{30}(12 + n_{30}) + N_{31}(4 + n_{31}) + N_{32}(8 + n_{32}) + N_{33}(12 + n_{33}) + N_{34}(4 + n_{34}) + N_{35}(8 + n_{35}) + N_{36}(12 + n_{36}) + N_{37}(4 + n_{37}) + N_{38}(8 + n_{38}) + N_{39}(12 + n_{39}) + a_1 \cdot N_{40}(4 + n_{40}) + a_2 \cdot N_{41}(4 + n_{41}) + b \cdot N_{42}(4 + n_{42}) + b \cdot N_{43}(8 + n_{43}) = 4N_{01} + 2N_{02} + N_{03} + (4 + x)N_{04} + 6N_{05} + 4N_{06} + 2N_{07} + N_{08}$$

$$f_3 = f(K) \\ N_{01} = N_4 \quad (15)$$

$$-6f_4 = 6f(SO_4) \\ 6N_{04} + 6N_{06} = 6N_5 + 6N_6 + 6N_9 + 6N_{14} + 12N_{15} + 6N_{28} + 6b \cdot N_{42} + 12b \cdot N_{43} \quad (16)$$

$$f_5 = f(Fe) \\ N_7 + N_8 + N_9 + N_{10} + N_{11} + N_{12} + 2N_{13} + N_{14} + N_{15} + N_{29} + N_{30} + N_{31} + N_{32} + N_{33} + a_1 \cdot N_{40} = N_{04} \quad (17)$$

$$f_6 = f(C) \\ 2N_{16} + 2N_{17} + 2N_{18} + N_{19} + N_{20} + N_{21} + 4N_{29} + 6N_{30} + 2N_{31} + 4N_{32} + 6N_{33} + 2N_{34} + 4N_{35} + 6N_{36} + 2N_{37} + 4N_{38} + 6N_{39} + 2a_1 \cdot N_{40} + 2a_2 \cdot N_{41} = N_{02} + 2N_{05} + N_{07} \quad (18)$$

$$f_7 = f(Mn) \\ N_{22} + N_{23} + N_{24} + N_{25} + N_{26} + N_{27} + N_{28} + N_{34} + N_{35} + N_{36} + N_{37} + N_{38} + N_{39} a_2 \cdot N_{41} + b \cdot N_{42} + b \cdot N_{43} = N_{01} \quad (19)$$

Note that the core balance $f(SO_4)$ is identical here with the S-elemental balance, $f(S) = f(SO_4)$. Then we get, by turns:

$$f_{12} = 2f_2 - f_1 \\ -N_2 + N_3 + 7N_5 + 8N_6 + N_8 + 8N_9 + N_{11} + 2N_{12} + 2N_{13} + 8N_{14} + 16N_{15} + 6N_{16} + 7N_{17} + 8N_{18} + 4N_{19} + 5N_{20} + 6N_{21} + 8N_{22} + 8N_{23} + N_{25} + N_{27} + 8N_{28} + 16N_{29} + 24N_{30} + 8N_{31} + 16N_{32} + 24N_{33} + 8N_{34} + 16N_{35} + 24N_{36} + 8N_{37} + 16N_{38} + 24N_{39} + 8a_1 \cdot N_{40} + 8a_2 \cdot N_{41} + 8b \cdot N_{42} + 8b \cdot N_{43} = 8N_{01} + 4N_{02} + 8N_{04} + 6N_{05} + 6N_{06} + 4N_{07} \quad (20)$$

$$f_0 + f_{12} - f_3 - 6f_4 \\ 2(N_7 + N_8 + N_9) + 3(N_{10} + N_{11} + N_{12} + 2N_{13} + N_{14} + N_{15}) + 6(N_{16} + N_{17} + N_{18}) + 4(N_{19} + N_{20} + N_{21}) + 7N_{22} + 6N_{23} + 3(N_{24} + N_{25}) + 2(N_{26} + 2N_{27} + 2N_{28}) + 14N_{29} + 20N_{30} + 9N_{31} + 15N_{32} + 21N_{33} + 8N_{34} + 14N_{35} + 20N_{36} + 9N_{37} + 15N_{38} + 21N_{39} + 8a_1 \cdot N_{40} + 8a_2 \cdot N_{41} + 3b \cdot N_{42} + 3b \cdot N_{43} = 7N_{01} + 4N_{02} + 2N_{04} + 6N_{05} + 4N_{07} \quad (21)$$

All the species involved only with fans (H, O, K and S) were cancelled ("filtered") within the linear combination (21). It also means that players are involved in each component and species of Eq. 21. The linear combination

$$Z_{Fe}f_5 + Z_Cf_6 + Z_{Mn}f_7 - (f_0 + f_{12} - f_3 - 6f_4)$$

is identical with Eq. 13. This way, the equivalence of the Approaches I and II to GEB is proved for the D+T system. For the simpler systems: D_1+T and D_2+T , this equivalence can be checked in a similar way. This means that the two Approaches (I and II) to GEB are mutually equivalent from mathematical viewpoint, i.e.,

$$\text{Approach I to GEB} \Leftrightarrow \text{Approach II to GEB.}$$

3.3. Modification of the Approach I to GEB

Only a part of electrons in players participate redox reactions. Having it in mind, on the basis of Eq. 13 we formulate the linear combination

$$Z_{Fe}f_5 + Z_Cf_6 + Z_{Mn}f_7 - (f_0 + f_{12} - f_3 - 6f_4) \\ (Z_{Fe}-2)(N_7 + N_8 + N_9) + (Z_{Fe}-3)(N_{11} + N_{12} + 2N_{13} + N_{14} + N_{15}) + 2(Z_C-3)(N_{16} + N_{17} + N_{18}) + (Z_C-4)(N_{19} + N_{20} + N_{21}) + (Z_{Mn}-7)N_{22} + (Z_{Mn}-6)N_{23} + (Z_{Mn}-3)(N_{24} + N_{25}) + (Z_{Mn}-2)(N_{26} + N_{27} + N_{28}) + (Z_{Fe} - 2 +$$

$$2 \cdot 2(Z_C - 3)) \cdot N_{29} + (Z_{Fe} - 2 + 3 \cdot 2(Z_C - 3)) \cdot N_{30} + (Z_{Fe} - 3 + 2(Z_C - 3)) \cdot N_{31} + (Z_{Fe} - 3 + 2 \cdot 2(Z_C - 3)) \cdot N_{32} + (Z_{Fe} - 3 + 3 \cdot 2(Z_C - 3)) \cdot N_{33} + (Z_{Mn} - 2 + 2(Z_C - 3)) \cdot N_{34} + (Z_{Mn} - 2 + 2 \cdot 2(Z_C - 3)) \cdot N_{35} + (Z_{Mn} - 2 + 3 \cdot 2(Z_C - 3)) \cdot N_{36} + (Z_{Mn} - 3 + 2(Z_C - 3)) \cdot N_{37} + (Z_{Mn} - 3 + 2 \cdot 2(Z_C - 3)) \cdot N_{38} + (Z_{Mn} - 3 + 3 \cdot 2(Z_C - 3)) \cdot N_{39} + a_1 \cdot (Z_{Fe} - 2 + 2(Z_C - 3)) \cdot N_{40} + a_2 \cdot (Z_{Mn} - 2 + 2(Z_C - 3)) \cdot N_{41} + b \cdot (Z_{Mn} - 3)(N_{42} + N_{43}) = (Z_{Fe} - 2) \cdot N_{04} + 2(Z_C - 3)N_{05} + (Z_C - 4)(N_{02} + N_{07}) + (Z_{Mn} - 7)N_{01} \quad (22)$$

where $Z_{Fe} \leq Z_{Fe}$, $Z_C \leq Z_C$, $Z_{Mn} \leq Z_{Mn}$. In particular, for $Z_{Fe} = 0$, $Z_C = 0$, $Z_{Mn} = 0$, we have the balance identical with $-(f_0 + f_{12} - f_3 - 6f_4)$, see Eq. 21. Incidentally, also $Z_{Fe} \geq Z_{Fe}$, $Z_C \geq Z_C$, $Z_{Mn} \geq Z_{Mn}$ is admitted here, from mathematical (not chemical!) viewpoint.

3.4. The simplest form of GEB for the D+T system

The f_{12} (Eq. 20) is the primary form of GEB, $f_{12} = pr$ -GEB, in the D+T system. The linear combination $f_{01234} = f_0 + f_{12} - f_3 - 6f_4$ gives the simpler/shorter form of GEB (Eq. 21), where only components and species with players are involved. Further, intentional combination of f_{01234} with the balances f_5 , f_6 , f_7 for players gives the simplest/shortest balance $f_{01234567}$ for GEB, with the smallest number of kinds of different components and species, where players are involved

$$f_{01234567} = 3f_5 + 4f_6 + 2f_7 - (f_0 + f_{12} - f_3 - 6f_4) \\ N_7 + N_8 + N_9 + 2(N_{16} + N_{17} + N_{18}) + 5N_{29} + 7N_{30} + 2N_{31} + 4N_{32} + 6N_{33} + 2N_{34} + 4N_{35} + 6N_{36} + N_{37} + 3N_{38} + 5N_{39} + 3a_1 \cdot N_{40} + 2a_2 \cdot N_{41} + 5N_{01} = N_{04} + 2N_{05} + 5N_{22} + 4N_{23} + (N_{24} + N_{25}) + b \cdot (N_{42} + N_{43}) \Rightarrow N_7 + N_8 + N_9 + 2(N_{16} + N_{17} + N_{18}) - (5N_{22} + 4N_{23} + (N_{24} + N_{25}) + b \cdot (N_{42} + N_{43})) + 5N_{29} + 7N_{30} + 2N_{31} + 4N_{32} + 6N_{33} + 2N_{34} + 4N_{35} + 6N_{36} + N_{37} + 3N_{38} + 5N_{39} + 3a_1 \cdot N_{40} + 2a_2 \cdot N_{41} = N_{04} + 2N_{05} - 5N_{01} \quad (23)$$

The carbonate components and species related to the CO_2 -admixture of D and T are not involved in Eq. 23. It also means that Eq. 23 is the shortest one, i.e. it contains (qualitatively) the smallest number of different components and species.

3.5. Linear combinations of balances for the D and T subsystems

Applying the notations (12), we formulate the charge and elemental/core balances for D and T, and their linear combinations.

The T subsystem

From (12) we have, by turns,

$$f_0 = ChB \\ N_2 - N_3 + N_4 - N_{20} - 2N_{21} - N_{22} = 0 \\ f_1 = f(H) \\ 2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + 2N_4n_4 + N_{19}(2 + 2n_{19}) + N_{20}(1 + 2n_{20}) + 2N_{21}n_{21} + 2N_{22}n_{22} = 2N_{03} \\ f_2 = f(O) \\ N_1 + N_2n_2 + N_3(1 + n_3) + N_4n_4 + N_{19}(3 + n_{19}) + N_{20}(3 + n_{20}) + N_{21}(3 + n_{21}) + N_{22}(4 + n_{22}) = 4N_{01} + 2N_{02} + N_{03} \\ f_{12} = 2f_2 - f_1 \\ -N_2 + N_3 + 4N_{19} + 5N_{20} + 6N_{21} + 8N_{22} = 8N_{01} + 4N_{02} \\ -f_3 = -f(K) \\ N_{01} = N_4 \\ -4f_{61} = -4f(CO_3) \\ 4N_{02} = 4N_{19} + 4N_{20} + 4N_{21} \\ -7f_7 = -7f(Mn)$$

$$7N_{01} = 7N_{22}$$

$$f_0 + f_{12} - f_3 - 4f_{61} - 7f_7$$

$$0 = 0$$

The D subsystem

From (12) we have, by turns,

$$f_0 = \text{ChB}$$

$$N_2 - N_3 - N_5 - 2N_6 + 2N_7 + N_8 - N_{17} - 2N_{18} - N_{20} - 2N_{21} - 2N_{29} - 4N_{30} - 2N_{35} - 4N_{36} = 0$$

$$f_1 = f(H)$$

$$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + N_5(1 + 2n_5) + 2N_6n_6 + 2N_7n_7 + N_8(1 + 2n_8) + 2N_9n_9 + N_{16}(2 + 2n_{16}) + N_{17}(1 + 2n_{17}) + 2N_{18}n_{18} + N_{19}(2 + 2n_{19}) + N_{20}(1 + 2n_{20}) + 2N_{21}n_{21} + 2N_{29}n_{29} + 2N_{30}n_{30} + 2a_1 \cdot N_{40}n_{40} = 2xN_{04} + 6N_{05} + 2N_{06} + 2N_{08}$$

$$f_2 = 2f(O)$$

$$N_1 + N_2n_2 + N_3(1 + n_3) + N_5(4 + n_5) + N_6(4 + n_6) + N_7n_7 + N_8(1 + n_8) + N_9(4 + n_9) + N_{16}(4 + n_{16}) + N_{17}(4 + n_{17}) + N_{18}(4 + 1n_{18}) + N_{19}(3 + n_{19}) + N_{20}(3 + n_{20}) + N_{21}(3 + n_{21}) + N_{29}(8 + n_{29}) + N_{30}(12 + 2n_{30}) + a_1 \cdot N_{40}(4 + n_{40}) = (4 + x)N_{04} + 6N_{05} + 4N_{06} + 2N_{07} + N_{08}$$

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

$$- N_2 + N_3 + 7N_5 + 8N_6 + N_8 + 8N_9 + 6N_{16} + 7N_{17} + 8N_{18} + 4N_{19} + 5N_{20} + 6N_{21} + 16N_{29} + 24N_{30} + 8a_1 \cdot N_{40} = 8N_{04} + 6N_{05} + 6N_{06} + 4N_{07}$$

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

$$6N_{04} + 6N_{06} = 6N_5 + 6N_6 + 6N_9$$

$$- 2f_5 = - 2f(Fe)$$

$$2N_{04} = 2N_7 + 2N_8 + 2N_9 + 2N_{29} + 2N_{30} + 2a_1 \cdot N_{40}$$

$$- 4f_{61} = - 4f(\text{CO}_3)$$

$$4N_{07} = 4N_{19} + 4N_{20} + 4N_{21}$$

$$- 6f_{62} = - 6f(\text{C}_2\text{O}_4)$$

$$6N_{05} = 6N_{16} + 6N_{17} + 6N_{18} + 12N_{29} + 18N_{30} + 6a_1 \cdot N_{40}$$

$$f_0 + f_{12} - 6f_4 - 2f_5 - 4f_{61} - 6f_{62}$$

$$0 = 0$$

3.6. The distinguishing role of $f_{12} = 2f(O) - f(H)$ in electrolytic systems

Intentional linear combination of the balances gives the identity $0 = 0$, for both non-redox subsystems: D and T, considered separately. This proves the linear dependency of the balances $f_0, f_{12}, f_3, f_{61}, f_7$ for T, and $f_0, f_{12}, f_4, f_5, f_{61}, f_{62}$ for D. This means that f_{12} is linearly dependent on the remaining balances for a given subsystem: $f_{12} = f_3 + 4f_{61} + 7f_7 - f_0$ for T, and $f_{12} = 6f_4 + 2f_5 + 4f_{61} + 6f_{62} - f_0$ for D. Consequently, f_{12} is not formulated in calculations related to non-redox systems.

The simplest/shortest form of linear combination for the redox D+T system is represented by the linear combination $f_{01234567} = 3f_5 + 4f_6 + 2f_7 - (f_0 + f_{12} - f_3 - 6f_4)$, Eq. 23. This linear combination is then different from the identity.

In general, the identity $0 = 0$ property is valid for any electrolytic non-redox system. The independence/dependence of f_{12} from charge ($f_0 = \text{ChB}$) and other elemental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) for different elements/cores Y_k is the general criterion distinguishing between redox and non-redox systems.^[21] Hence, a redox system is formulated by the set of K independent balances $f_0, f_{12}, f_3, \dots, f_k$, whereas the set of $K-1$ independent balances f_0, f_3, \dots, f_k is used to describe a non-redox system.

3.7. Validity of the $I = B + L + 1$ relationship for electrolytic (sub)systems

The simple general relation $I = B + L + 1$ between the number I of kinds of species, the number B of balances composed of charge balance and independent elemental/core balances and the number L of independent equilibrium constants related to electrolytic systems, was suggested in^[26]; $L = K$ for a redox system and $L = K-1$ for a non-redox system.

This relationship will be confirmed here for the redox D+T system, specified above. Namely, we have:

- at $a_1 = a_2 = b = 1$: $I = 43$; $B = 6$ ($f_0, f_{12}, f(S), f(C), f(Fe), f(Mn)$); $L = 36 \rightarrow 43 = 6 + 36 + 1$;
- at $a_1 = a_2 = 1, b = 0$: $I = 41$; $B = 6$; $L = 34 \rightarrow 41 = 6 + 34 + 1$;
- at $a_1 = 1, a_2 = 0, b = 0$: $I = 40$; $B = 6$; $L = 33 \rightarrow 40 = 6 + 33 + 1$;
- at $a_1 = 0, a_2 = 1, b = 0$: $I = 40$; $B = 6$; $L = 33 \rightarrow 40 = 6 + 33 + 1$;
- at $a_1 = a_2 = b = 0$: $I = 39$; $B = 6$; $L = 32 \rightarrow 39 = 6 + 32 + 1$.

Any (soluble or precipitated) complex species specified in (12) relates to its equilibrium constant; therefore, an increase in I is related to an increase in L .

3.8. Equations for the D+T System in terms of concentrations

Applying the relations:

$$x_i^{Z_i} \cdot (V_0 + V) = 10^3 \cdot \frac{N_i}{N_A}, C_{01}V_0 = 10^3 \cdot N_{04}/N_A, C_{02}V_0 = 10^3 \cdot N_{05}/N_A, C_{03}V_0 = 10^3 \cdot N_{06}/N_A, C_{04}V_0 = 10^3 \cdot N_{07}/N_A, CV = 10^3 \cdot N_{01}/N_A, C_1V = 10^3 \cdot N_{02}/N_A$$

$$(24)$$

in Eq. 13, we obtain the equation for GEB, written in terms of molar concentrations as follows:

$$F_{(I)} = (Z_{Fe} - 2)([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) + (Z_{Fe} - 3)([Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + Fe(SO_4)_2^{-1}) + (Z_{Fe} - 2 + 4 \cdot (Z_C - 3))[Fe(C_2O_4)_2^{-2}] + (Z_{Fe} - 2 + 6 \cdot (Z_C - 3))[Fe(C_2O_4)_3^{-4}] + (Z_{Fe} - 3 + 2 \cdot (Z_C - 3))[FeC_2O_4^{+1}] + (Z_{Fe} - 3 + 4 \cdot (Z_C - 3))[Fe(C_2O_4)_2^{-1}] + (Z_{Fe} - 3 + 6 \cdot (Z_C - 3))[Fe(C_2O_4)_3^{-3}] + 2(Z_C - 3)([H_2C_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) + (Z_C - 4)([H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}]) + (Z_{Mn} - 7)[MnO_4^{-1}] + (Z_{Mn} - 6)[MnO_4^{-2}] + (Z_{Mn} - 3)([Mn^{+3}] + [MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] + [Mn(SO_4)_2^{-1}])) + (Z_{Mn} - 3 + 2 \cdot (Z_C - 3))[MnC_2O_4^{+1}] + (Z_{Mn} - 3 + 4 \cdot (Z_C - 3))[Mn(C_2O_4)_2^{-1}] + (Z_{Mn} - 3 + 6 \cdot (Z_C - 3))[Mn(C_2O_4)_3^{-3}] + (Z_{Mn} - 2)([Mn^{+2}] + [MnOH^{+1}] + [MnSO_4]) + (Z_{Mn} - 2 + 2 \cdot (Z_C - 3))[MnC_2O_4] + (Z_{Mn} - 2 + 4 \cdot (Z_C - 3))[Mn(C_2O_4)_2^{-2}] + (Z_{Mn} - 2 + 6 \cdot (Z_C - 3))[Mn(C_2O_4)_3^{-4}] + a_1 \cdot (Z_{Fe} - 2 + 2 \cdot (Z_C - 3))[FeC_2O_4] + a_2 \cdot (Z_{Mn} - 2 + 2 \cdot (Z_C - 3))[MnC_2O_4] - ((Z_{Fe} - 2)C_{01}V_0 + 2 \cdot (Z_C - 3)C_{02}V_0 + (Z_C - 4)(C_{04}V_0 + C_1V) + (Z_{Mn} - 7)CV)/(V_0 + V) = 0$$

$$(13a)$$

Applying the relations (24) in Eq. 23, we get the shortest form of GEB

$$F_{(II)} = [Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] + 2([H_2C_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) - (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + ([Mn^{+3}] + [MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] + [Mn(SO_4)_2^{-1}])) + 5[Fe(C_2O_4)_2^{-2}] + 7[Fe(C_2O_4)_3^{-4}] + 2[FeC_2O_4^{+1}] + 4[Fe(C_2O_4)_2^{-1}] + 6[Fe(C_2O_4)_3^{-3}] + 2[MnC_2O_4] + 4[Mn(C_2O_4)_2^{-2}] + 6[Mn(C_2O_4)_3^{-4}] + [MnC_2O_4^{+1}] + 3[Mn(C_2O_4)_2^{-1}] + 5[Mn(C_2O_4)_3^{-3}] + 3a_1 \cdot [FeC_2O_4] + 2a_2 \cdot [MnC_2O_4] - (C_{01}V_0 + 2C_{02}V_0 - 5CV)/(V_0 + V) = 0$$

$$(23a)$$

Moreover, we write the equation for charge balance:

$$F_0 = [H^{+1}] - [OH^{-1}] + CV/(V_0+V) - [HSO_4^{-1}] - 2[SO_4^{-2}] - [HC_2O_4^{-1}] - 2[C_2O_4^{-2}] - [MnO_4^{-1}] - 2[MnO_4^{-2}] + 3[Mn^{+3}] + 2[MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] - [Mn(SO_4)_2^{-1}]) + [MnC_2O_4^{+1}] - [Mn(C_2O_4)_2^{-1}] - 3[Mn(C_2O_4)_3^{-3}] + 2[Mn^{+2}] + [MnOH^{+1}] + b \cdot ([MnSO_4^{+1}] - [Mn(SO_4)_2^{-1}]) - 2[Mn(C_2O_4)_2^{-2}] - 4[Mn(C_2O_4)_3^{-4}] + 2[Fe^{+2}] + [FeOH^{+1}] - 2[Fe(C_2O_4)_2^{-2}] - 4[Fe(C_2O_4)_3^{-4}] + 3[Fe^{+3}] + 2[FeOH^{+2}] + [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] - [Fe(SO_4)_2^{-1}] + [FeC_2O_4^{+1}] - [Fe(C_2O_4)_2^{-1}] - 3[Fe(C_2O_4)_3^{-3}] = 0 \quad (14a)$$

and equations for concentration balances:

$$F_4 = HSO_4^{-1} + [SO_4^{-2}] + [MnSO_4] + [FeSO_4] + [FeSO_4^{+1}] + 2[Fe(SO_4)_2^{-1}] + b \cdot ([MnSO_4^{+1}] + 2[Mn(SO_4)_2^{-1}]) - (C_{01} + C_{03})V_0/(V_0+V) = 0 \quad (16a)$$

$$F_5 = [Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] + [Fe(C_2O_4)_2^{-2}] + [Fe(C_2O_4)_3^{-4}] + [Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}] + [FeC_2O_4^{+1}] + [Fe(C_2O_4)_2^{-1}] + [Fe(C_2O_4)_3^{-3}] + a_1 \cdot [FeC_2O_4] - C_{01}V_0/(V_0+V) = 0 \quad (17a)$$

$$F_6 = 2[H_2C_2O_4] + 2[HC_2O_4^{-1}] + 2[C_2O_4^{-2}] + [H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] + 2[MnC_2O_4^{+1}] + 4[Mn(C_2O_4)_2^{-1}] + 6[Mn(C_2O_4)_3^{-3}] + 2[MnC_2O_4] + 4[Mn(C_2O_4)_2^{-2}] + 6[Mn(C_2O_4)_3^{-4}] + 4[Fe(C_2O_4)_2^{-2}] + 6[Fe(C_2O_4)_3^{-4}] + 2[FeC_2O_4^{+1}] + 4[Fe(C_2O_4)_2^{-1}] + 6[Fe(C_2O_4)_3^{-3}] + 2a_1 \cdot [FeC_2O_4] + 2a_2 \cdot [MnC_2O_4] - (2C_{02}V_0 + C_{04}V_0 + C_1V)/(V_0+V) = 0 \quad (18a)$$

$$F_7 = [MnO_4^{-1}] + [MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] - [Mn(SO_4)_2^{-1}]) + [MnC_2O_4^{+1}] + [Mn(C_2O_4)_2^{-1}] + [Mn(C_2O_4)_3^{-3}] + [Mn^{+2}] + [MnOH^{+1}] + [MnSO_4] + [MnC_2O_4] + [Mn(C_2O_4)_2^{-2}] + [Mn(C_2O_4)_3^{-4}] + a_2 \cdot [MnC_2O_4] - CV/(V_0+V) = 0 \quad (19a)$$

In this context, the relation

$$[K^{+1}] = CV/(V_0+V) \quad (15a)$$

obtained from (15) is considered as an equality, not equation (concentration balance), because at defined C, V₀ and V values, it is a number and – as such – it can enter immediately the charge balance (14a). *Nota bene*, an equation includes at least two different species involved in it.

In Equations 17a – 19a, we have a₁ = 0 if FeC₂O₄ is not the equilibrium solid phase, and a₂ = 0 if MnC₂O₄ is not the equilibrium solid phase, i.e., values of the related solubility products are not crossed.

On the basis of the equations derived for the D+T system KMnO₄ + CO₂ ⇌ FeSO₄ + H₂C₂O₄ + H₂SO₄ + CO₂ one can formulate the balances for simpler systems: KMnO₄ + CO₂ ⇌ FeSO₄ + H₂C₂O₄ + H₂SO₄ + CO₂ (D₁+T system), and KMnO₄ + CO₂ ⇌ H₂C₂O₄ + H₂SO₄ + CO₂ (D₂+T system), For modeling purposes, one can also assume C₁ = C₀₄ = 0.

Equations for the D₁+T system

At C₀₂ = 0, from Equations 13a, 23a, 14a, 16a, 17a, 18a, 19a we obtain, by turns,

$$F_{(I)} = (Z_{Fe} - 2)([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) + (Z_{Fe} - 3)([Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}]) + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}] + (Z_{C-4})([H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}]) + (Z_{Mn-7})[MnO_4^{-1}] +$$

$$(Z_{Mn-6})[MnO_4^{-2}] + (Z_{Mn-3})([Mn^{+3}] + [MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] + [Mn(SO_4)_2^{-1}])) + (Z_{Mn-2})([Mn^{+2}] + [MnOH^{+1}] + [MnSO_4]) - ((Z_{Fe-2})C_{01}V_0 + (Z_{C-4})(C_{04}V_0 + C_1V) + (Z_{Mn-7})CV)/(V_0+V) = 0 \quad (13b)$$

$$F_{(II)} = [Fe_{+2}] + [FeOH_{+1}] + [FeSO_4] - (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + ([Mn^{+3}] + [MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] + [Mn(SO_4)_2^{-1}])) - (C_{01}V_0 - 5CV)/(V_0+V) = 0 \quad (23b)$$

$$F_0 = [H^{+1}] - [OH^{-1}] + CV/(V_0+V) - [HSO_4^{-1}] - 2[SO_4^{-2}] - [MnO_4^{-1}] - 2[MnO_4^{-2}] + 3[Mn^{+3}] + 2[MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] - [Mn(SO_4)_2^{-1}]) + 2[Mn^{+2}] + [MnOH^{+1}] + 2[Fe^{+2}] + [FeOH^{+1}] + 3[Fe^{+3}] + 2[FeOH^{+2}] + [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] - [Fe(SO_4)_2^{-1}] = 0 \quad (14b)$$

and equations for concentration balances:

$$F_4 = [HSO_4^{-1}] + [SO_4^{-2}] + [FeSO_4] + [FeSO_4^{+1}] + 2[Fe(SO_4)_2^{-1}] + [MnSO_4] + b \cdot ([MnSO_4^{+1}] + 2[Mn(SO_4)_2^{-1}]) - (C_{01}V_0 + C_{03}V_0)/(V_0+V) = 0 \quad (16b)$$

$$F_5 = [Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] + [Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}] - C_{01}V_0/(V_0+V) = 0 \quad (17b)$$

$$F_6 = [H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] - (C_{04}V_0 + C_1V)/(V_0+V) = 0 \quad (18b)$$

$$F_7 = [MnO_4^{-1}] + [MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}] + [Mn^{+2}] + [MnOH^{+1}] + [MnSO_4] + b \cdot ([MnSO_4^{+1}] + [Mn(SO_4)_2^{-1}]) - CV/(V_0+V) = 0 \quad (19b)$$

Equations for the D₂+T system

At C₀₁ = 0, from Equations 13a, 23a, 14a, 16a, 18a, 19a we obtain, by turns,

$$F_{(I)} = 2(Z_{C-3})([H_2C_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) + (Z_{C-4})([H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}]) + (Z_{Mn-7})[MnO_4^{-1}] + (Z_{Mn-6})[MnO_4^{-2}] + (Z_{Mn-3})([Mn^{+3}] + [MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] + [Mn(SO_4)_2^{-1}])) + (Z_{Mn-3} + 2 \cdot (Z_{C-3}))[MnC_2O_4^{+1}] + (Z_{Mn-3} + 4 \cdot (Z_{C-3}))[Mn(C_2O_4)_2^{-1}] + (Z_{Mn-3} + 6 \cdot (Z_{C-3}))[Mn(C_2O_4)_3^{-3}] + (Z_{Mn-2})([Mn^{+2}] + [MnOH^{+1}] + [MnSO_4]) + (Z_{Mn-2} + 2 \cdot (Z_{C-3}))[MnC_2O_4] + (Z_{Mn-2} + 4 \cdot (Z_{C-3}))[Mn(C_2O_4)_2^{-2}] + (Z_{Mn-2} + 6 \cdot (Z_{C-3}))[Mn(C_2O_4)_3^{-4}] + a_2 \cdot (Z_{Mn-2} + 2 \cdot (Z_{C-3}))[MnC_2O_4] - (2 \cdot (Z_{C-3})C_{02}V_0 + (Z_{C-4})(C_{04}V_0 + C_1V) + (Z_{Mn-7})CV)/(V_0+V) = 0 \quad (13c)$$

$$F_{(II)} = 2([H_2C_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) - (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + ([Mn^{+3}] + [MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] + [Mn(SO_4)_2^{-1}])) + 2[MnC_2O_4] + 4[Mn(C_2O_4)_2^{-2}] + 6[Mn(C_2O_4)_3^{-4}] + [MnC_2O_4^{+1}] + 3[Mn(C_2O_4)_2^{-1}] + 5[Mn(C_2O_4)_3^{-3}] + 2a_2 \cdot [MnC_2O_4] - (2C_{02}V_0 - 5CV)/(V_0+V) = 0 \quad (23c)$$

$$F_0 = [H^{+1}] - [OH^{-1}] + [K^{+1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] - [HC_2O_4^{-1}] - 2[C_2O_4^{-2}] - [MnO_4^{-1}] - 2[MnO_4^{-2}] + 3[Mn^{+3}] + 2[MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] - [Mn(SO_4)_2^{-1}]) + [MnC_2O_4^{+1}] - [Mn(C_2O_4)_2^{-1}] - 3[Mn(C_2O_4)_3^{-3}] + 2[Mn^{+2}] + [MnOH^{+1}] + b \cdot ([MnSO_4^{+1}] - [Mn(SO_4)_2^{-1}]) - 2[Mn(C_2O_4)_2^{-2}] - 4[Mn(C_2O_4)_3^{-4}] + 2[Fe^{+2}] + [FeOH^{+1}] - 2[Fe(C_2O_4)_2^{-2}] - 4[Fe(C_2O_4)_3^{-4}] + 3[Fe^{+3}] + 2[FeOH^{+2}] + [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] - [Fe(SO_4)_2^{-1}] + [FeC_2O_4^{+1}] - [Fe(C_2O_4)_2^{-1}] - 3[Fe(C_2O_4)_3^{-3}] = 0 \quad (14c)$$

and equations for concentration balances:

$$F_4 = [HSO_4^{-1}] + [SO_4^{-2}] + [MnSO_4] + b \cdot ([MnSO_4^{+1}] + 2[Mn(SO_4)_2^{-1}]) - C_{03}V_0/(V_0+V) = 0 \quad (16c)$$

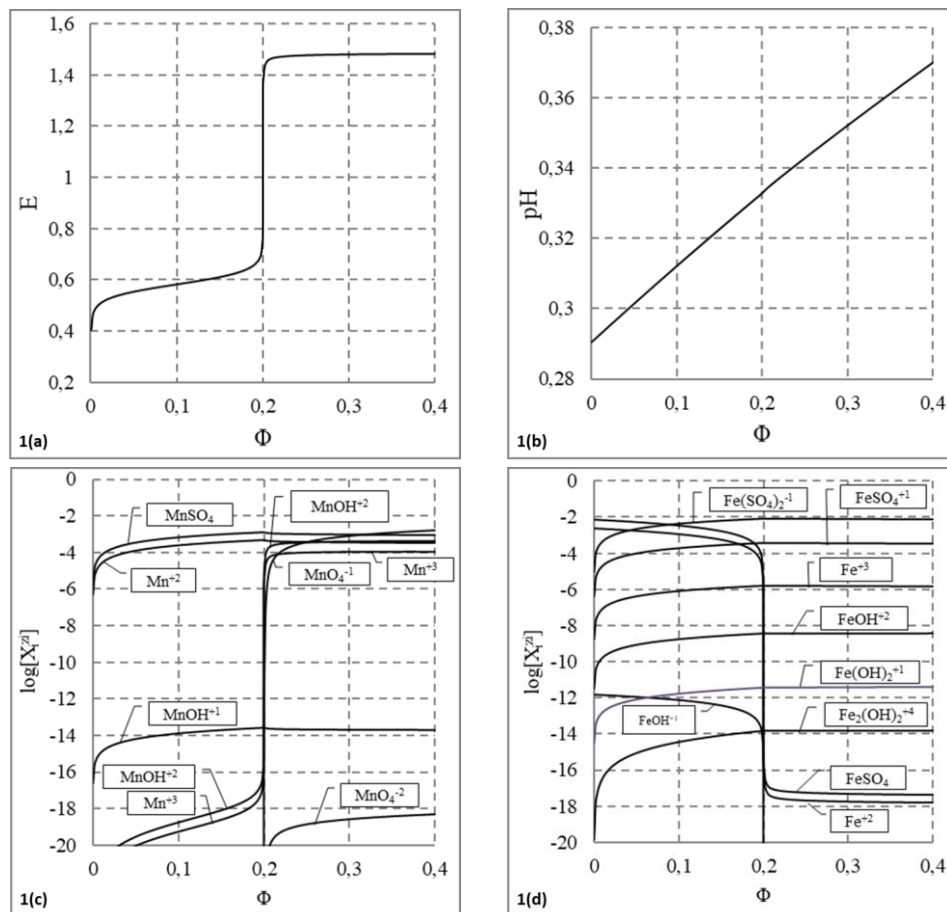


Fig. 1. Graphs for the D₁+T system, $\Phi = CV/C_{01}V_0$.

$$F_6 = 2[H_2C_2O_4] + 2[HC_2O_4^{-1}] + 2[C_2O_4^{-2}] + [H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] + 2[MnC_2O_4^{+1}] + 4[Mn(C_2O_4)_2^{-1}] + 6[Mn(C_2O_4)_3^{-3}] + 2[MnC_2O_4] + 4[Mn(C_2O_4)_2^{-2}] + 6[Mn(C_2O_4)_3^{-4}] + 2a_2 \cdot [MnC_2O_4] - (2C_{02}V_0 + C_{04}V_0 + C_1V)/(V_0+V) = 0 \quad (18c)$$

$$F_7 = [MnO_4^{-1}] + [MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}] + b \cdot ([MnSO_4^{+1}] + [Mn(SO_4)_2^{-1}] + [MnC_2O_4^{+1}] + [Mn(C_2O_4)_2^{-1}] + [Mn(C_2O_4)_3^{-3}] + [Mn^{+2}] + [MnOH^{+1}] + [MnSO_4] + [MnC_2O_4] + [Mn(C_2O_4)_2^{-2}] + [Mn(C_2O_4)_3^{-4}] + a_2 \cdot [MnC_2O_4] - CV/(V_0+V) = 0 \quad (19a)$$

3.9. The set of equilibrium constants

Concentrations of the species in F_(i) or F_(ii), and F₀, F₄, F₅, F₆, F₇ of the D+T system, enter the relationships for equilibrium constants, [26] listed below.

$$[OH^{-1}] = 10^{pH-14}; [HSO_4^{-1}] = 10^{1.8-pH} \cdot [SO_4^{-2}]; [H_2C_2O_4] = 10^{5.2-2pH} \cdot [C_2O_4^{-2}]; [HC_2O_4^{-1}] = 10^{3.8-pH} \cdot [C_2O_4^{-2}]; [H_2CO_3] = 10^{16.4-2pH} \cdot [CO_3^{-2}]; [HCO_3^{-1}] = 10^{10.1-pH} \cdot [CO_3^{-2}]; [FeOH^{+1}] = 10^{4.5} \cdot [Fe^{+2}][OH^{-1}]; [FeOH^{+2}] = 10^{11.0} \cdot [Fe^{+3}][OH^{-1}]; [Fe(OH)_2^{+1}] = 10^{21.7} \cdot [Fe^{+3}][OH^{-1}]^2; [Fe_2(OH)_2^{+4}] = 10^{25.1} \cdot [Fe^{+3}]^2[OH^{-1}]^2; [MnOH^{+1}] = 10^{3.4} \cdot [Mn^{+2}][OH^{-1}]; [FeSO_4] = 10^{2.3} \cdot [Fe^{+2}][SO_4^{-2}]; [FeSO_4^{+1}] = 10^{4.18} \cdot [Fe^{+3}][SO_4^{-2}]; [Fe(SO_4)_2^{-1}] = 10^{7.4} \cdot [Fe^{+3}][SO_4^{-2}]^2; [MnSO_4] = 10^{2.28} \cdot [Mn^{+2}][SO_4^{-2}]; [Fe(C_2O_4)_2^{-2}] = 10^{4.52} \cdot [Fe^{+2}][C_2O_4^{-2}]^2; [Fe(C_2O_4)_3^{-4}] = 10^{5.22} \cdot [Fe^{+2}][C_2O_4^{-2}]^3; [FeC_2O_4^{+1}] = 10^{7.53} \cdot [Fe^{+3}][C_2O_4^{-2}]; [Fe(C_2O_4)_2^{-1}] = 10^{13.64} \cdot [Fe^{+3}][C_2O_4^{-2}]^2; [Fe(C_2O_4)_3^{-3}] = 10^{18.49} \cdot [Fe^{+3}][C_2O_4^{-2}]^3; [MnC_2O_4] = 10^{3.82} \cdot [Mn^{+2}][C_2O_4^{-2}]; [Mn(C_2O_4)_2^{-2}] = 10^{5.25} \cdot [Mn^{+2}][C_2O_4^{-2}]^2; [Mn(C_2O_4)_3^{-3}] = 10^{9.98} \cdot [Mn^{+3}][C_2O_4^{-2}];$$

$$[Mn(C_2O_4)_2^{-1}] = 10^{16.57} \cdot [Mn^{+3}][C_2O_4^{-2}]^2; [Mn(C_2O_4)_3^{-3}] = 10^{19.42} \cdot [Mn^{+3}][C_2O_4^{-2}]^3$$

Applying $A = F/(RT \cdot \ln 10) = 16.9$ for $T = 298$ K, we obtain:

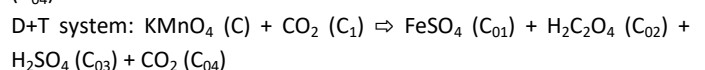
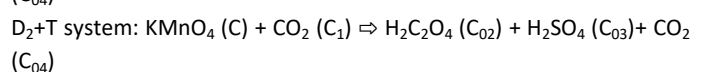
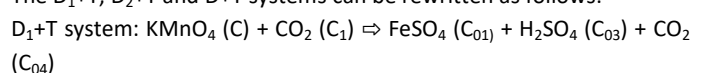
$$[MnO_4^{-1}] = [Mn^{+2}] \cdot 10^{5A(E-1.507)+8pH}; [MnO_4^{-2}] = [Mn^{+2}] \cdot 10^{4A(E-1.743)+8pH}; [Mn^{+3}] = [Mn^{+2}] \cdot 10^{A(E-1.509)}; [Fe^{+3}] = [Fe^{+2}] \cdot 10^{A(E-0.771)}; [H_2CO_3] = [H_2C_2O_4] \cdot 10^{A(E+0.396)+pH}.$$

The solubility products for FeC₂O₄ and MnC₂O₄ are as follows: $K_{s01} = [Fe^{+2}][C_2O_4^{-2}] = 10^{-6.7}$, $K_{s02} = [Mn^{+2}][C_2O_4^{-2}] = 10^{-5.3}$.

The appropriate subsets of these relationships refer to the D₁+T and D₂+T systems. The complete set of independent equilibrium constants provides the quantitative thermodynamic knowledge on the related system.

3.10. Specification of the systems tested

The D₁+T, D₂+T and D+T systems can be rewritten as follows:



where: $V_0 = 100$, $C = 0.1$, $C_{01} = C_{02} = 0.01$, $C_{03} = 0.5$, $C_1 = C_{04} = 0.001$.

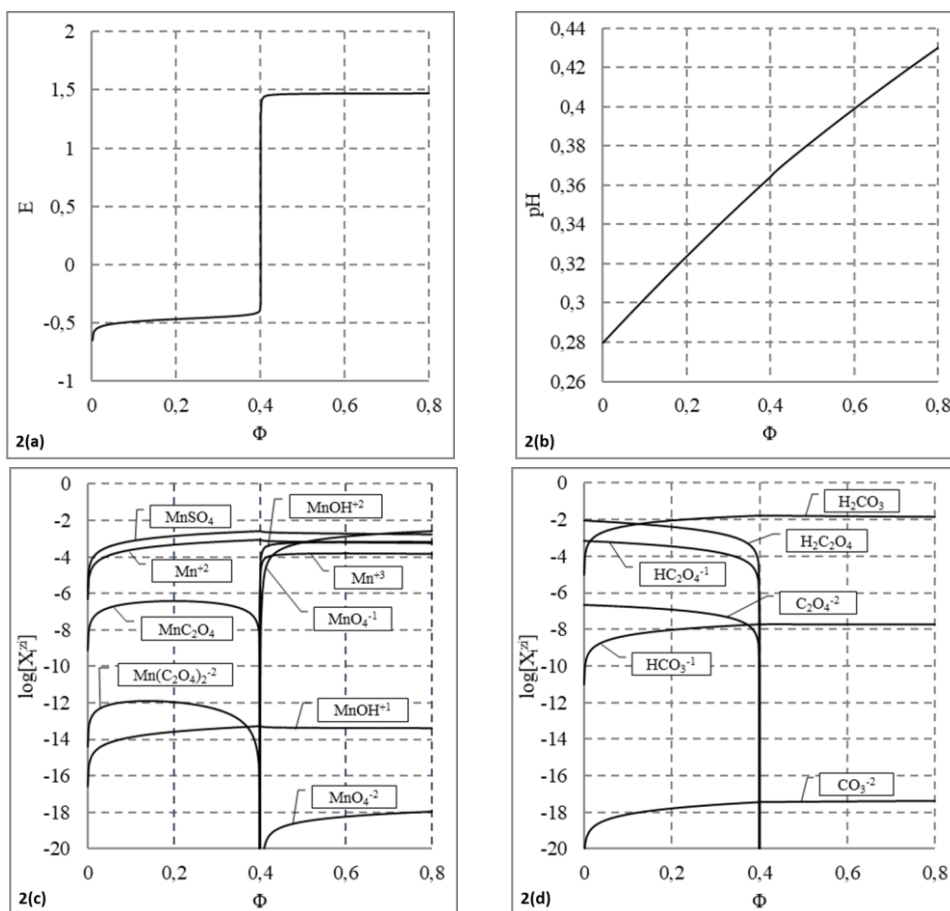


Fig. 2. Graphs for the D_2+T system, $\Phi = CV/C_{O_2}V_0$.

3.11. Independent variables and calculation procedure

In all the systems tested, the set of $K=6$ independent variables $x_k = x_k(V)$ ($k=1, \dots, 6$) were assumed:

$$x_1 = \text{pH}, x_2 = E, x_3 = -\log[\text{Mn}^{+2}], x_4 = -\log[\text{Fe}^{+2}], x_5 = -\log[\text{H}_2\text{CO}_3], x_6 = -\log[\text{SO}_4^{-2}];$$

where $\text{pH} = -\log[\text{H}^{+1}]$, $[e^{-1}] = 10^{-A.E}$. These variables constitute the vector $x = x(V) = [x_1, \dots, x_6]^T$. In all instances, the number of the variables equals to the number of balances. The variables $x_k = x_k(V)$ referred to concentrations $x_i^{z_i}$ are then introduced as the negative powers of 10, e.g. $[\text{H}^{+1}] = 10^{-\text{pH}}$, $[e^{-1}] = 10^{-A.E}$. In this context, the calculation procedure, made according to iterative computer program MATLAB,^[12] volume V is taken as the steering variable.

3.12. Graphical presentation of results

On this basis of results thus obtained, one can plot the functions: $E = E(V)$, $\text{pH} = \text{pH}(V)$ and speciation curves $\log[x_i^{z_i}] = \vartheta_i(V)$. If a single analyte is included in the titrand, as in the case of $D_1 + T$ and $D_2 + T$ systems, we can use the fraction titrated

$$\Phi = \frac{c \cdot V}{c_0 \cdot V_0} \quad (25)$$

on the abscissa; it provides a kind of normalization in the plots thus obtained.

The graphs of: E vs. Φ , pH vs. Φ relationships and speciation curves $\log[x_i^{z_i}]$ vs. Φ are plotted in Figures 2a,b,c,d and 3a,b,c,d. The graphs of: E vs. V , pH vs. V relationships and speciation curves $\log[x_i^{z_i}]$ vs. V are plotted in Fig. 4. Potential E in NHE scale and the value $b = 0$, see (12), were assumed here.

Graphs for the D_1+T System

The graphs of (1a) $E = E(\Phi)$, (1b) $\text{pH} = \text{pH}(\Phi)$ and speciation curves $\log[x_i^{z_i}] = \vartheta_i(\Phi)$ (1c, 1d), obtained for the D_1+T system, are plotted in Fig. 1, where $\Phi = \frac{CV}{C_{O_1}V_0}$.

Graphs for the D_2+T System

The graphs of (2a) $E = E(\Phi)$, (2b) $\text{pH} = \text{pH}(\Phi)$ and speciation curves $\log[x_i^{z_i}] = \vartheta_i(\Phi)$ (2c, 2d), obtained for the D_2+T system, are plotted in Fig. 2, where $\Phi = \frac{CV}{C_{O_2}V_0}$.

Graphs for the $D+T$ System

The graphs of (3a) $E = E(V)$, (3b) $\text{pH} = \text{pH}(V)$ and speciation curves $\log[x_i^{z_i}] = \vartheta_i(V)$ (3c, 3d), obtained for the $D+T$ system, are plotted in Fig. 3.

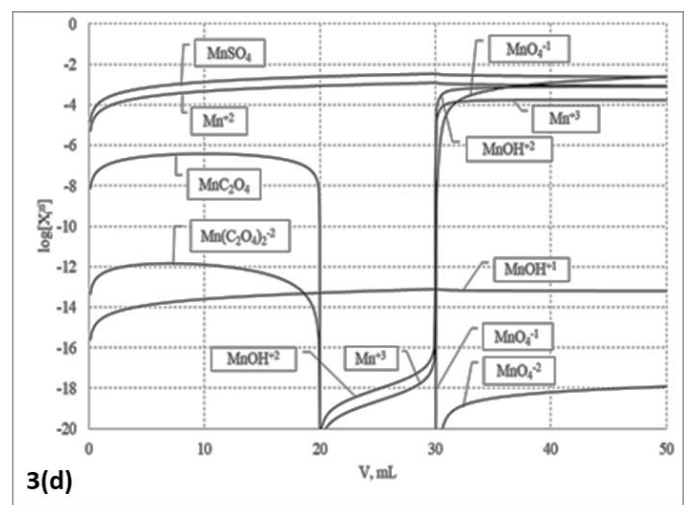
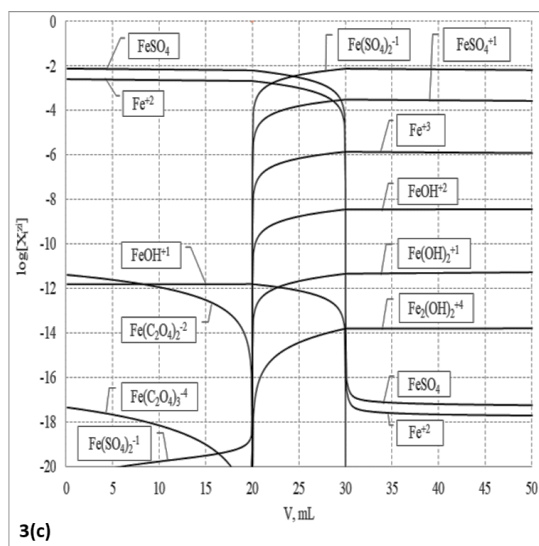
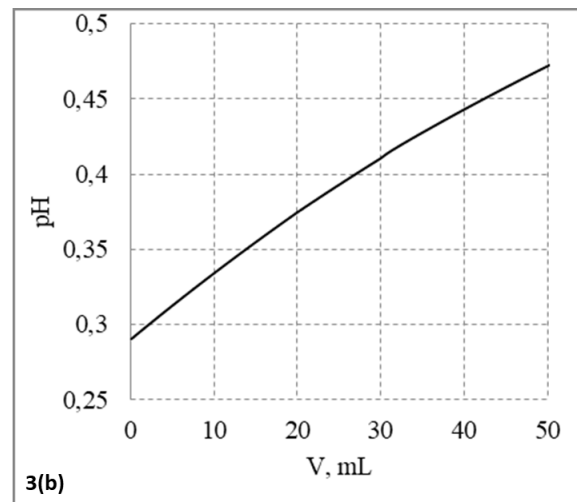
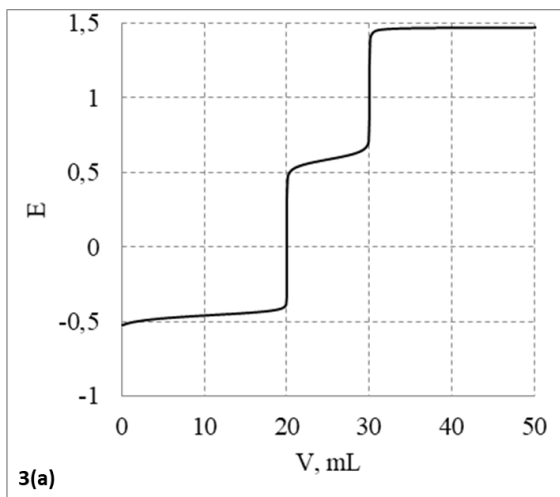


Fig. 3. Graphs for the D+T system.

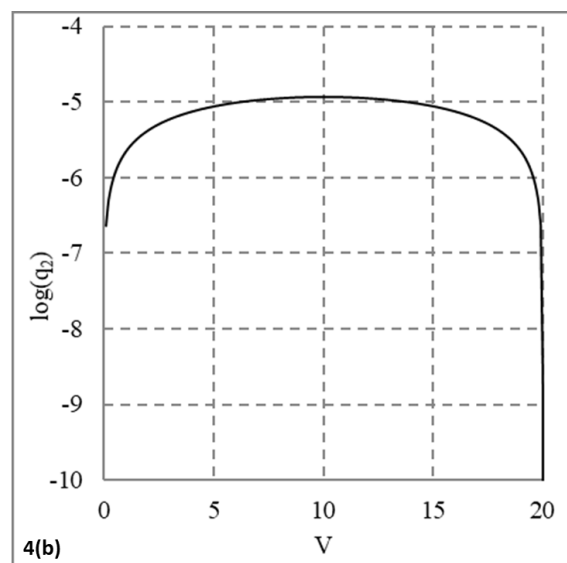
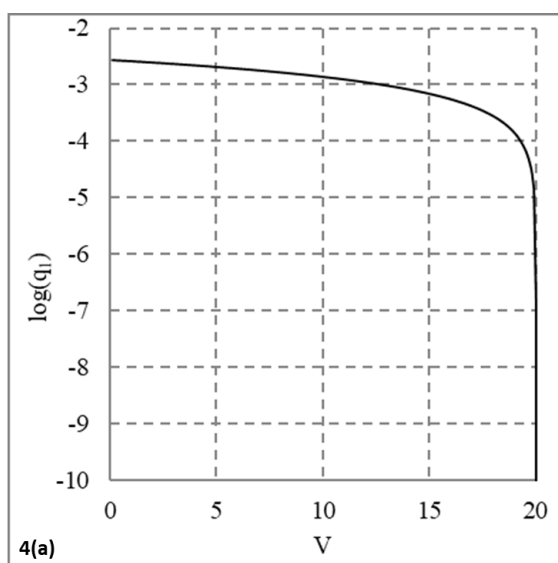


Fig. 4. The $\log(q_i)$ vs. V relationships (Eq. 26) plotted in the D+T system for: (4a) Fe and (4b) Mn oxalates; $b=0$.

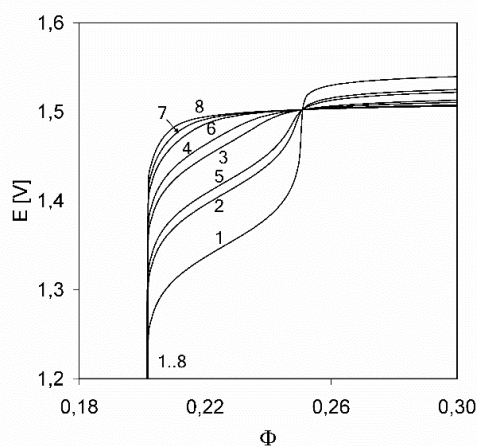


Fig. 5. Fragments of hypothetical titration curves for the D_1+T system, plotted for different (presumed) pairs of (K_1, K_2) values for the stability constants of $Mn(SO_4)^{+3-2i}$ complexes: 1 - $(10^4, 10^7)$, 2 - $(10^3, 10^6)$, 3 - $(10^{2.5}, 10^5)$, 4 - $(10^2, 10^4)$, 5 - $(10^4, 0)$, 6 - $(10^3, 0)$, 7 - $(10^2, 0)$, 8 - $(0, 0)$.^[4]

3.13. Are the oxalates precipitated?

To check the possibility of formation of the precipitates: FeC_2O_4 and/or MnC_2O_4 , the relationships: $\log q_1$ vs. V and $\log q_2$ vs. V were formulated, where:

$$q_1 = \frac{[Fe^{+2}][C_2O_4^{-2}]}{K_{s01}} \text{ and } q_2 = \frac{[Mn^{+2}][C_2O_4^{-2}]}{K_{s02}} \quad (26)$$

From Fig. 4 we see that $\log(q_i) < 0$ ($i = 1, 2$), i.e. the products: $[Fe^{+2}][C_2O_4^{-2}]$ and $[Mn^{+2}][C_2O_4^{-2}]$ do not attain the related values: K_{s01} and K_{s02} , i.e., the precipitates do not exist in the $D+T$ and D_2+T systems as equilibrium solid phases, i.e. $a_1=a_2=0$.

3.14. Doubts about the completeness of the set of equilibrium constants

Fragments of hypothetical titration curves for the D_1+T system, are plotted in Fig. 5 for different pairs of (K_1, K_2) values of the stability constants for the presumed $Mn(SO_4)_i^{+3-2i}$ complexes, $[Mn(SO_4)_i^{+3-2i}] = K_i[Mn^{+3}][SO_4^{-2}]^i$ ($i = 1, 2$), and indicated at the corresponding lines.^[3]

3.15. Generalized equivalence mass (GEM)

The main task of a titration is the estimation of the equivalent volume V_{eq} , corresponding to the volume V of T , where the fraction titrated Φ (Eq. 25) assumes the value

$$\Phi_{eq} = \frac{C \cdot V_{eq}}{C_0 \cdot V_0} \quad (27)$$

In contradistinction to visual titrations, where the end volume $V_e \cong V_{eq}$ is registered, all instrumental titrations aim, in principle, to obtain the V_{eq} value on the basis of experimental data $\{(V_j, y_j) \mid j=1, \dots, N\}$, where $y = pH$ or E for potentiometric methods of analysis. We have

$$C_0 \cdot V_0 = 10^3 \cdot \frac{m_A}{M_A} \quad (28)$$

where $m_A [g]$ and $M_A \left[\frac{g}{mol} \right]$ denote mass and molar mass of analyte (A), respectively. From Eqs. 25 and 28, we get

$$m_A = 10^{-3} \cdot C \cdot M_A \cdot \frac{V}{\Phi} \quad (29)$$

The value of the fraction $\frac{V}{\Phi}$ in Eq. 29, obtained from Eq. 25

$$\frac{V}{\Phi} = \frac{C_0 \cdot V_0}{C} \quad (30)$$

is constant during the titration. Particularly, at the end (e) and equivalent (eq) points we have

$$\frac{V}{\Phi} = \frac{V_e}{\Phi_e} = \frac{V_{eq}}{\Phi_{eq}} \quad (31)$$

The V_e [mL] value is the volume of T consumed up to the end (e) point, where the titration is terminated (ended). The V_e value is usually determined in visual titration, when a pre-assumed color (or color change) of $D+T$ mixture is obtained. In a visual acid-base titration, pH_e value corresponds to the volume V_e [mL] of T added from the very start of the titration, and

$$\Phi_e = \frac{C \cdot V_e}{C_0 \cdot V_0} \quad (32)$$

is the Φ -value related to the end point. From Eqs. 29 and 31, one obtains:

$$a) m_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_e} \text{ and } b) m_A = 10^{-3} \cdot C \cdot V_{eq} \cdot \frac{M_A}{\Phi_{eq}} \quad (33)$$

This does not mean that we may choose between Eqs. 33a and 33b, to calculate m_A . That is, Eq. 33a cannot be applied for the evaluation of m_A : V_e is known, but Φ_e unknown. Calculation of Φ_e needs prior knowledge of C_0 value; However C_0 is unknown before the titration; otherwise, the titration would be purposeless. Also Eq. 33b is useless: the 'round' Φ_{eq} value is known exactly, but V_{eq} is unknown; V_e (not V_{eq}) is determined in visual titrations.

Because Eqs. 34a and 36b appear to be useless, the third, approximate formula for m_A , has to be applied,^[8] namely:

$$m'_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_{eq}} \Rightarrow m'_A = 10^{-3} \cdot C \cdot V_e \cdot R_A^{eq} \quad (34)$$

where Φ_{eq} is put for Φ_e in Eq. 33a, and

$$R_A^{eq} = \frac{M_A}{\Phi_{eq}} \quad (35)$$

is named as the equivalent mass (GEM). The relative error in accuracy, resulting from this substitution, equals to

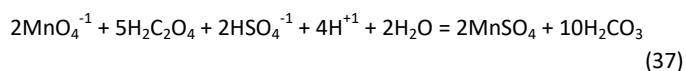
$$\delta = \frac{m'_A - m_A}{m_A} = \frac{m'_A}{m_A} - 1 = \frac{V_e}{V_{eq}} - 1 = \frac{\Phi_e}{\Phi_{eq}} - 1 \quad (36)$$

Table 1. Some points (V_j , E_j) from the vicinity of jumps on the curve $E = E(V)$ in Fig. 3a.

| V_e [mL] | E_e [V] | V_e [mL] | E_e [V] |
|------------|-----------|------------|-----------|
| 19.8 | -0.4002 | 29.8 | 0.6844 |
| 19.9 | -0.3912 | 29.9 | 0.7024 |
| 19.999 | -0.3320 | 29.99991 | 0.8827 |
| 19.9995 | -0.3231 | 29.99995 | 0.8978 |
| 19.9999 | -0.3025 | 29.99999 | 0.9391 |
| 20 | -0.2382 | 30 | 1.0430 |
| 20.0001 | 0.2881 | 30.00001 | 1.1600 |
| 20.0005 | 0.3294 | 30.00005 | 1.2013 |
| 20.001 | 0.3472 | 30.0001 | 1.2191 |
| 20.1 | 0.4657 | 30.1 | 1.3967 |

Some data obtained for the D+T system are collected in Table 1. For the point $(V_e, E_e) = (19.9, 0.3912)$ we have $\delta = 19.9/20.00 - 1 = -0.5\%$.

The $\Phi = \Phi_{eq} = C \cdot V_{eq} / C_{02} \cdot V_0 = 0.4$ value ($2:5 = 0.4$), expected on the basis of equation



corresponds to the equivalence volume $V_{eq} = 20$ (Table 1), where an abrupt growth in potential (E) value occurs (Fig. 2a, 3a). Relatively small change in pH value (Fig. 2b) is involved with (i) high buffer capacity of the titrand D, (ii) reaction (37), where protons are attached as substrates, and (iii) dilution effect.

Concentration of CO_2 formed in this system exceeds the solubility of CO_2 in strongly acidified aqueous media; then $10\text{H}_2\text{CO}_3 \rightarrow 10\text{CO}_2 + 10\text{H}_2\text{O}$. Carbonate and oxalate species are involved in a single concentration balance (Eqs. 18a, 18c), i.e., they cannot be formulated in separate balances.

3.16. A remark concerning water clusters

When formulating the balances: f_1 and f_2 for any, redox or non-redox system, one can take into account the formation of water clusters $(\text{H}_2\text{O})_\lambda(N_{1\lambda}, \lambda = 1, 2, \dots)$ in aqueous solutions. Writing these balances as follows:

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

$$2 \cdot \sum_{\lambda=1}^{\Lambda} \lambda \cdot N_{1\lambda} + N_2(1 + 2n_2) + N_3(1 + 2n_3) + \dots$$

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

$$\sum_{\lambda=1}^{\Lambda} \lambda \cdot N_{1\lambda} + N_2(1 + n_2) + N_3(1 + n_3) + \dots$$

we have:

$$f_{12} = 2f_2 - f_1 \\ - N_2 + N_3 + \dots$$

i.e., all components related to water clusters and water molecules in components and species are cancelled here.

3.17. Final comments

The GATES/GEB provides the best thermodynamic formulation of electrolytic redox systems of any degree of complexity, namely: equilibrium, non-equilibrium and metastable, mono- and poly-phase, static and dynamic electrolytic systems in aqueous, non-aqueous and mixed-solvent media, and liquid-liquid extraction systems. The GEB concept is perceived as an emanation of the elements conservation, as the general law of Nature. The GEB concept, unknown before 1992, related to electrolytic redox systems completes the set of equations needed for quantitative description of an electrolytic redox system. Earlier/other thermodynamic approaches to these systems are thus invalidated.

Two equivalent Approaches (I, II) to GEB are presented. Equivalency of these Approaches is evidenced also in the systems considered herein. The Approach I is based on a card-game principle. The Approach II is based on the linear combination $f_{12} = 2 \cdot f(\text{O}) - f(\text{H})$ of elemental balances: $f_1 = f(\text{H})$ for $Y_1 = \text{H}$, and $f_2 = f(\text{O})$ for $Y_2 = \text{O}$. Linear independency/dependency of f_{12} from charge ($f_0 = \text{ChB}$) and other elemental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) is the general criterion distinguishing between redox and non-redox systems.

The GEB formulated according to GATES/GEB principles Approach I to GEB can be applied if the oxidation numbers for all elements in components forming a system and in species of the system are known beforehand. The Approach II to GEB needs none prior information on oxidation numbers of all elements in components forming the system, and the species in the system. Within the Approaches I and II, the roles of oxidants and reductants are not ascribed to components and particular species.

The calculations are related to closed systems, separated from its environment by diathermal walls. Some limitations resulting from the impossibility of meeting these conditions in real laboratory practice were also marked here.

4. Conclusions

As a continuation of the information contained in the epilogue for ^[55], one can state that 30 years have passed since the discovery of GATES/GEB. In the context of the critical opinion, expressed (verbally and graphically) in ^[53,55], we observe gibberish as a means of communication between people, and chemists in particular. The case was so transparent that everyone smashed his head on it. This is evidenced by the fact that the quotations of GATES/GEB principle in the Internet are related only to the papers of its creator. Often one should say firmly "no!" to express one's beliefs.

In ^[14,55], the GEB was perceived by us in context with GATES like a lotus flower. Paraphrasing a Chinese proverb, one can state that "The lotus flower (GEB), lotus leaves (charge and elemental/core balances) and lotus seed (species) come from the same root (fundamental laws of preservation)". It's worth mentioning, that lotus is among three plants on the planet able to regulate its own temperature and to produce heat through the thermoregulation process. Isn't it, incidentally, an analogy to thermal stability as one of the conditions ensuring the invariability of the equilibrium constants in the titration process?

Conflicts of Interest

The authors declare no conflict of interest.

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