Physicochemical and analytical implications of GATES, GEB and GEM

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ABSTRACT

The fundamental property of electrolytic systems 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 $Y_2 = O$, is presented. The dependency/independency of the f_{12} on charge balance (f_0 = ChB) and other elemental and/or core balances $f_k = f(Y_k)$ (k=3,…,K) is the general criterion distinguishing between non-redox and redox systems. The f_{12} related to a redox system is the primary form of a Generalized Electron Balance (GEB), formulated for redox systems within the Generalized Approach to Electrolytic System (GATES) as GATES/GEB ⊂ GATES. The set of K balances $f_0,f_{12},f_3,\dots,f_K$ is necessary/sufficient/needed to solve an electrolytic redox system, while the K-1 balances $f_0,f_3,\dots,f_K$ are the set applied to solve an electrolytic non-redox system. The identity (0 = 0) procedure of checking the linear independency/dependency property of f_{12} within the set $f_0,f_{12},f_3,\dots,f_K$ (*i*) provides the criterion distinguishing between the redox and non-redox systems and (*ii*) specifies oxidation numbers (ONs) of elements in particular components of the system, and in the species formed in the system. Some chemical concepts, perceived as derivative within GATES, are indicated.

Keywords: Modeling of electrolytic systems; GATES; GEB; GATES/GEB, GEM.

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Introduction

Redox systems are the most important and the most complex type of electrolytic systems, when formulated for thermodynamic purposes. The transfer of electrons is usually accompanied there by other (acid-base, complexation and precipitation) reactions. The complexity of redox systems is expressed by the number of equilibrium constants, and by diversity of these constants involved with the system considered. In all instances, it is important to provide a consistent thermodynamic approach, where the systems of different complexity are elaborated in a uniform manner according to Generalized Approach to Electrolytic System (GATES) principles formulated (Michałowski, 2011). When related to redox systems, the acronym GATES/GEB (Michałowska-Kaczmarczyk and Michałowski, 2014) is applied; GATES/GEB ⊂ GATES, where the Generalized Electron Balance (GEB), discovered by Michałowski and formulated as the Approaches I (1992) and II (2005) to GEB, is involved.

The GEB is fully compatible with charge and concentration balances, and relations for the corresponding equilibrium constants. The *GATES/GEB* is perceived as the best possible thermodynamic approach (Michałowska-Kaczmarczyk and Michałowski, 2020), as the new paradigm and the unique tool applicable to redox systems and GEB is considered as the Law of Nature (Michałowska-Kaczmarczyk et al., 2017). GEB completes the set of K equations needed for mathematical description of redox systems, on the basis of calculations made according to an iterative computer program.Both Approaches to GEB are equivalent, i.e.,

Approach I to GEB ⇔ Approach II to GEB

In other words, both Approaches (I, II) to GEB are mutually transformable, according to linear combination procedure (Michałowska-Kaczmarczyk and Michałowski, 2018).

The Approach I to GEB, based on the principle of a common pool of electrons, is involved with electron-active elements, perceived (in convention of 'card game') as players; electron-non-active elements are termed as fans, and electrons as 'money'. The 'money' is introduced into the system by players. The terms: players, fans and money are then applied as parities/analogy to redox systems.

The Approach II to GEB originates from the linear combination $f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(O) - f(H)$ of elemental balances: $f_1 = f(H)$ for H, and $f_2 = f(O)$ for O, formulated for a redox system. For a non-redox system, $2 \cdot f(O) - f(H)$ is a linear combination of charge balance f_0 = ChB, and other elemental/core balances $f_k = f(Y_k)$ (k=3,…,K), where $Y_k \neq$ H, O. For a redox system, $f_0, f_{12}, f_3, \ldots, f_K$ is a set of K linearly independent balances, whereas for a non-redox system we have the set of K – 1 linearly independent balances $f_0, f_3, \ldots, f_K$, i.e. f_1 and f_2, and then $f_{12} = 2 \cdot f_2 - f_1$ are not involved in the set of balances related to a non-redox system. Then linear dependency or independency of f_{12} and $f_0, f_3, \ldots, f_K$ distinguishes between redox or non-redox systems [44-51].In a non-redox system, only fans ('lookers-on') are involved within the set of balances $f_0, f_3, \ldots, f_K$.

A core is considered as a cluster of different atoms with defined composition (expressed by chemical formula), structure and external charge, unchanged in the system in question. For example, SO_4^{-2} is a core within different sulfate species in the set (1) specified below.

The Approach II, when compared with the Approach I, offers several advantages Although derivation of GEB according to the Approach II is more laborious (time-consuming), it enables to formulate this balance without prior knowledge of oxidation numbers (ONs) for the elements, involved in opponents forming a system, and in species of the system thus formed. The composition (expressed by chemical formula) of the components and species, together with their external charges, are required; it provides an information sufficient to formulate the GEB. It is the paramount advantage of the Approach II to GEB over the Approach I to GEB, where prior knowledge of ON's is needed. Anyway, the ON – representing the degree of oxidation of an element in a compound and in a species – is a contractual concept. In this regard, formulation of GEB according to Approach II is far more useful than the Approach I, particularly when applied to complex organic species in redox systems of biological origin, where radical and ion-radical species are formed (Wybraniec et al., 2013).

What is more, the players and fans, as ones perceived from the Approach I viewpoint, are not indicated *a priori* within the Approach II. The Approach I, considered as a "short" version of GEB, is more convenient when oxidation numbers for all elements of the system are known beforehand. Within the Approach II to GEB, the roles of oxidants and reductants are not ascribed *a priori*to particular components forming the redox system, and to the species formed in this system. In other words, full 'democracy' is established *a priori* within GATES/GEB, where oxidation number, oxidant, reductant, equivalent mass, and stoichiometric reaction notation are the redundant concepts only. The fact that $f_{12} = 2 \cdot f(O) - f(H)$ is the primary form of GEB indicates clearly the exquisite role of H and O in redox systems, especially in aspect of insignificantly small concentrations of free electrons, as those calculated and discussed. All other(earlier and more contemporary) approaches of other authors to formulation of electrolytic redox systems were also reviewed and thoroughly criticized/disqualified (Michalowski et al., 2015) .

Formulation of redox systems with kinetic effects involved was presented. A three phase (liquid-liquid+solid) extraction redox system was formulated. The GATES/GEB formulation for relatively simple redox systems is provided by references (Meija et al., 2017).

The dynamic buffer capacity for redox systems, the concept formulated first by Michałowski is similar - in its external form - to that proposed by him for acid-base systems, of different complexity (Toporek et al., 2014).

The GATES/GEB formulation was also applied for analytical purposes, namely for Gran (I and II) methods modified purposefully for redox and non-redox systems. The formulation based on the Approach II principle was applied for electrolytic systems in mixed-solvent media. Some examples of more acceptable formulation of redox systems according to stoichiometric principles are provided (Michałowski et al., 2014).

The GATES, and GATES/GEB in particular, provide very important regularities unknown in earlier literature, where the key role was ascribed to stoichiometric notation. GATES provides a deep insight into the nature of the investigated system. Among others, it enables to formulate the Generalized Equivalence Mass (GEM) concept, with none reference to a stoichiometric notation.

Preliminary assumptions and notation

For modeling purposes, realized according to *GATES principles*, we assume a closed system,

matter $\not\Leftrightarrow$ system/subsystems $\Leftrightarrow$ heat

separated from its environment by diathermal(freely permeable by heat) *walls* as boundaries, preventing (⇎) thematter *(e.g.* H_2O, CO_2, O_2,…*)* exchange but allowing (⇔) the exchange of heat, resulting from exo- or endothermic processes occurred in the system (Michałowski, 2011).

The energies of chemical reactions are much smaller than energies of nuclear or thermonuclear (fusion) transformations, where the mass change Δm resulting from an energy ΔE evolved in these reactions is measurable, when estimated according to the formula $\Delta E = \Delta m \cdot c^2$. In chemical reactions, even for reaction $H_{2(g)} + 0.5O_{2(g)} = H_2O_{(l)}$ ($\Delta H^o = -286$ kJ/mol H_2O), the mass change equal $\Delta m = \Delta H^o/c^2 = -3.18 \cdot 10^{-9}$ g, is negligible (not measurable) when compared with 18 g of H_2O; (g) – gas, (l) – liquid (phase). Neutralization, hydration, hydrolysis or dilution phenomena give much smaller heat effects.

The closed systems are an approximation of open systems tested in common, laboratory practice. In modeling of such systems, it is assumed that an effect of the matter (e.g. H_2O, CO_2, O_2) exchange with the environment is negligibly small during the period designed for a chemical operation, such as titration T ⇨ D, perceived as a dynamic process, where titrant T (titrating solution) is added in successive portions into titrand D (solution titrated); D and T are subsystems of the D+T system thus formed. The energy exchange between the D+T system and the environment allows the titration to be performed under isothermal conditions. The temperature stability of the D+T system is, in turn, one of the preliminary conditions ensuring stability of the corresponding equilibrium constants. The titration is considered here as a quasistatic process realized in aqueous medium*, under isothermal conditions.*

The terms: components of the D and T subsystems and species in the D+T system are distinguished. After mixing the components, a mixture of defined species is formed. Thus the components form D and T, and the species enter the D+T system thus formed. The components and species are involved in the related balances.

It is justifiable to start the balancing from the numbers of particular entities: N_{0j} – for components (j = 1,…,J) represented by H_2O and solutes, and N_i – for species (ions and molecules) of i-th kind $X_i^{z_i} \cdot n_{iW}$ (i = 1,…,I), where I is the number of kinds of the species. The mono- or two-phase electrolytic system thus obtained involve N_1 molecules of H_2O and N_i species of i-th kind, $X_i^{z_i} \cdot n_{iW}$ (i=2, 3,…,I), specified briefly as $X_i^{z_i}$ (N_i, n_i), where $n_i \equiv n_{iW} \equiv n_iH_2O$. For ordering purposes, we write: H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3),… , i.e., $z_2 = 1$, $z_3 = -1$, … . The$X_i^{z_i}$'s, with different numbers of H_2O molecules involved in $X_i^{z_i} \cdot n_{iW}$, e.g. H^{+1}, H_3O^{+1} and $H_9O_4^{+1}$; $H_4IO_6^{-1}$, IO_4^{-1}; $H_2BO_3^{-1}$, $B(OH)_4^{-1}$; AlO_2^{-1}, $Al(OH)_4^{-1}$; $Fe(OH)_3$ and FeOOH, are considered equivalently, i.e., as the same species in this medium. The $n_i = n_{iW} = n_iH_2O$ values are virtually unknown – even for $X_2^{z_2} = H^{+1}$ in aqueous media, and depend on ionic strength (I) of the solution.

We address to aqueous media, whose species $X_i^{z_i}$ will be considered in their natural/factual form, i.e., as hydrates $X_i^{z_i} \cdot n_{iW}$, where z_i is a charge of this species (z_i = 0, ±1, ±2,…), 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, $n_i = n_{iW}$.

Static and dynamic systems are distinguished here. A s*tatic system is obtained after a disposable mixing s*pecific chemical compounds as solutes, and water as solvent. *A d*ynamic system can be realized according to titrimetric mode, where V mL of titrant T, added in successive portions into V_0 mL of titrand D, and V_0+V mL of D+T mixture is obtained at this point of the titration, if the volumes are additive; D and T are subsystems of the D+T system.

A dynamic redox D+T system composed of non-redox subsystems D and T

We consider here non-redox subsystems:

(1) D (V_0) subsystem, composed of $FeSO_4 \cdot 7H_2O$ (N_{05}) + H_2SO_4 (N_{06}) + H_2O (N_{07}) + CO_2 (N_{08}); (2) T (V) subsystem, composed of $Ce(SO_4)_2 \cdot xH_2O$ (N_{01}) + H_2SO_4 (N_{02}) + H_2O (N_{03}) + CO_2 (N_{04});
and (3) D+T (V_0+V) redox system, 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}), Ce^{+4} (N_{18}, n_{18}), $CeOH^{+3}$ (N_{19}, n_{19}), $Ce_2(OH)_3^{+5}$ (N_{20}, n_{20}), $Ce_2(OH)_4^{+4}$ (N_{21}, n_{21}), $CeSO_4^{+2}$ (N_{22}, n_{22}), $Ce(SO_4)_2$ (N_{23}, n_{23}), $Ce(SO_4)_3^{-2}$ (N_{24}, n_{24}), Ce^{+3} (N_{25}, n_{25}), $CeOH^{+2}$(N_{26}, n_{26}), $CeSO_4^{+1}$ (N_{27}, n_{27}), $Ce(SO_4)_2^{-1}$ (N_{28}, n_{28}), $Ce(SO_4)_3^{-3}$ (N_{29}, n_{29}) (1)

For example, the notation HSO_4^{-1} (N_4, n_4) applied here refers to N_4 ions $HSO_4^{-1}\cdot n_4H_2O$ involving: $N_4(1+2n_4)$ atoms of H, $N_4(4+n_4)$ atoms of O, and N_4 atoms of S.

The presence of CO_2 in T and D, considered here as an admixture from air, imitates real conditions of the analysis, on the step of preparation of D and T; the titration $T(V) \Rightarrow D(V_0)$ is realized in the closed system, under isothermal conditions. 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. The volume V_0+V mL of D+T system/mixture is obtained, if the assumption of additivity in the volumes is valid/tolerable. To avoid (possible) disturbances, the common notation (subscripts) assumed in the set (1) 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.

Formulation of balances for D, T and D+T

The D subsystem

We have here the balances:

f_0 = ChB

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

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_9n_9 + N_{10}(1+2n_{10}) + 2N_{11}n_{11} = 14N_{05} + 2N_{06} + 2N_{07}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_9n_9 + N_{10}(1+n_{10}) + N_{11}(4+n_{11}) = 11N_{05} + 4N_{06} + N_{07} + 2N_{08}$

$-f_3 = -f(SO_4)$

$N_{05} + N_{06} = N_4 + N_5 + N_{11}$

$-f_4 = -f(CO_3)$

$N_{08} = N_6 + N_7 + N_8$

$-f_5 = -f(Fe)$

$N_{05} = N_9 + N_{10} + N_{11}$

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

$-N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} = 8N_{05} + 6N_{06} + 4N_{08}$

The linear combination

$$f_{12} - 6\cdot f_3 - 4\cdot f_4 - 2\cdot f_5 = 0 \quad (2)$$

as the simple sum of collected balances:

$-N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} = 8N_{05} + 6N_{06} + 4N_{08}$

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

$6N_{05} + 6N_{06} = 6N_4 + 6N_5 + 6N_{11}$

$4N_{08} = 4N_6 + 4N_7 + 4N_8$

$2N_{05} = 2N_9 + 2N_{10} + 2N_{11}$

is transformed into identity, 0 = 0.

The balance (2) can be rewritten into equivalent forms

$$2\cdot f_2 - f_1 + f_0 - 6\cdot f_3 - 4\cdot f_4 - 2\cdot f_5 = 0 \mid \cdot(-1) \Leftrightarrow (+1)\cdot f_1 + (-2)\cdot f_2 + (+6)\cdot f_3 + (+4)\cdot f_4 + (+2)\cdot f_5 - f_0 = 0 \Leftrightarrow (+1)\cdot f(H) + (-2)\cdot f(O) + (+6)\cdot f(SO_4) + (+4)\cdot f(CO_3) + (+2)\cdot f(Fe) - ChB = 0 \quad (3)$$

where the coefficients/multipliers for the related balances are equal to ON's for all elements in the combined balances.

The T subsystem

We have here the balances:

f_0 = ChB

$N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 4N_{18} + 3N_{19} + 5N_{20} + 4N_{21} + 2N_{22} - 2N_{24} = 0$

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_{18}n_{18} + N_{19}(1+2n_{19}) + N_{20}(3+2n_{20}) + N_{21}(4+2n_{21}) + 2N_{22}n_{22} + 2N_{23}n_{23} + 2N_{24}n_{24} = 2xN_{01} + 2N_{02} + 2N_{03}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_{18}n_{18} + N_{19}(1+n_{19}) + N_{20}(3+n_{20}) + N_{21}(4+n_{21}) + N_{22}(4+n_{22}) + N_{23}(8+n_{23}) + N_{24}(12+n_{24})$
$= (8+x)N_{01} + 4N_{02} + N_{03} + 2N_{04}$

$-f_3 = -f(SO_4)$

$2N_{01} + N_{02} = N_4 + N_5 + N_{22} + 2N_{23} + 3N_{24}$

$-f_4 = -f(CO_3)$

$N_{04} = N_6 + N_7 + N_8$

$-f_6 = -f(Ce)$

$N_{01} = N_{18} + N_{19} + 2N_{20} + 2N_{21} + N_{22} + N_{23} + N_{24}$

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

$-N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{19} + 3N_{20} + 4N_{21} + 8N_{22} + 16N_{23} + 24N_{24}$
$= 16N_{01} + 6N_{02} + 4N_{04}$

The linear combination

$$f_{12} + f_0 - 6\cdot f_3 - 4\cdot f_4 - 4\cdot f_6 = 0 \quad (4)$$

as the simple sum of collected balances:

$-N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{19} + 3N_{20} + 4N_{21} + 8N_{22} + 16N_{23} + 24N_{24}$
$= 16N_{01} + 6N_{02} + 4N_{04}$

$N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 4N_{18} + 3N_{19} + 5N_{20} + 4N_{21} + 2N_{22} - 2N_{24} = 0$

$12N_{01} + 6N_{02} = 6N_4 + 6N_5 + 6N_{22} + 12N_{23} + 18N_{24}$

$4N_{04} = 4N_6 + 4N_7 + 4N_8$

$4N_{01} = 4N_{18} + 4N_{19} + 8N_{20} + 8N_{21} + 4N_{22} + 4N_{23} + 4N_{24}$

is transformed into identity, i.e., 0 = 0. The balance

(4) can be rewritten into equivalent forms:

$2\cdot f_2 - f_1 + f_0 - 6\cdot f_3 - 4\cdot f_4 - 4\cdot f_5 = 0 \ \ |\cdot(-1) \ \Leftrightarrow \ (+1)\cdot f_1 + (-2)\cdot f_2 + (+6)\cdot f_3 + (+4)\cdot f_4 + (+4)\cdot f_5 - f_0 = 0 \ \Leftrightarrow$

$(+1)\cdot f(H) + (-2)\cdot f(O) + (+6)\cdot f(SO_4) + (+4)\cdot f(CO_3) + (+4)\cdot f(Ce) - ChB = 0$ (5)

where the coefficients/multipliers for the related balances are equal to ON's for elements in the combined balances.

The D+T system

For the D+T system we have the balances:

$f_0 = ChB$

$N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 2N_9 + N_{10} + 3N_{12} + 2N_{13} + N_{14} + 4N_{15} + N_{16} - N_{17} + 4N_{18} + 3N_{19} + 5N_{20} + 4N_{21} + 2N_{22} - 2N_{24} + 3N_{25} + 2N_{26} + N_{27} - N_{28} - 3N_{29} = 0$ (6)

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_9n_9 + N_{10}(1+2n_{10}) + 2N_{11}n_{11} + 2N_{12}n_{12} + N_{13}(1+2n_{13}) + N_{14}(2+2n_{14}) + N_{15}(2+2n_{15}) + 2N_{16}n_{16} + 2N_{17}n_{17} + 2N_{18}n_{18} + + N_{19}(1+2n_{19}) + N_{20}(3+2n_{20}) + N_{21}(4+2n_{21}) + 2N_{22}n_{22} + 2N_{23}n_{23} + 2N_{24}n_{24} + 2N_{25}n_{25} + N_{26}(1+2n_{26}) + 2N_{27}n_{27} + 2N_{28}n_{28} + 2N_{29}n_{29} = 2xN_{01} + 2N_{02} + 2N_{03} + 14N_{05} + 2N_{06} + 2N_{07}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_9n_9 + N_{10}(1+n_{10}) + N_{11}(4+n_{11}) + N_{12}n_{12} + N_{13}(1+n_{13}) + N_{14}(2+n_{14}) + N_{15}(2+n_{15}) + N_{16}(4+n_{16}) + N_{17}(8+n_{17}) + N_{18}n_{18} + N_{19}(1+n_{19}) + N_{20}(3+n_{20}) + N_{21}(4+n_{21}) + N_{22}(4+n_{22}) + N_{23}(8+n_{23}) + N_{24}(12+n_{24}) + N_{25}n_{25} + N_{26}(1+n_{26}) + N_{27}(4+n_{27}) + N_{28}(8+n_{28}) + N_{29}(12+n_{29}) = (8+x)N_{01} + 4N_{02} + N_{03} + 2N_{04} + 11N_{05} + 4N_{06} + N_{07} + 2N_{08}$

$-f_3 = -f(SO_4)$

$2N_{01} + N_{02} + N_{05} + N_{06} = N_4 + N_5 + N_{11} + N_{16} + 2N_{17} + N_{22} + 2N_{23} + 3N_{24} + N_{27} + 2N_{28} + 3N_{29}$ (7)

$-f_4 = -f(CO_3)$

$N_{04} + N_{08} = N_6 + N_7 + N_8$ (8)

$-f_6 = -f(Ce)$

$N_{01} = N_{18} + N_{19} + 2N_{20} + 2N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + N_{26} + N_{27} + N_{28} + N_{29}$ (9)

$-f_5 = -f(Fe)$

$N_{05} = N_9 + N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17}$ (10)

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

$-N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} + N_{13} + 2N_{14} + 2N_{15} + 8N_{16} + 16N_{17} + N_{19} + 3N_{20} + 4N_{21} + 8N_{22} + 16N_{23} + 24N_{24} + N_{26} + 8N_{27} + 16N_{28} + 24N_{29} = 16N_{01} + 6N_{02} + 4N_{04} + 8N_{05} + 6N_{06} + 4N_{08}$ (11)

The linear combination

$f_{12} + f_0 - 6f_3 - 4f_4 = 0 \ \Leftrightarrow \ (+1)\cdot f_1 + (-2)\cdot f_2 + (+6)\cdot f_3 + (+4)\cdot f_4 - f_0 = 0 \ \Leftrightarrow$

$(+1)\cdot f(H) + (-2)\cdot f(O) + (+6)\cdot f(SO_4) + (+4)\cdot f(CO_3) - ChB = 0$ (12)

involving $K^*=4$ elemental/core balances for electron-non-active elements (fans): H, O, S, C is as follows:

$f_0 + f_{12} - 6f_3 - 4f_4$

$2(N_9+N_{10}+N_{11}) + 3(N_{12}+N_{13}+N_{14}+2N_{15}+N_{16}+N_{17}) + 4(N_{18}+N_{19}+2N_{20}+2N_{21}+N_{22}+N_{23}+N_{24}) + 3(N_{25}+N_{26}+N_{27}+N_{28}+N_{29}) = 2N_{05} + 4N_{01}$ (13)

Denoting atomic numbers: $Z_{Fe} = 26$, $Z_{Ce} = 58$, from Equations: 9, 10 and 13, we obtain the balance

$Z_{Fe}\cdot f_5 + Z_{Ce}\cdot f_6 - (2\cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4)$

$(Z_{Fe}-2)\cdot(N_9+N_{10}+N_{11}) + (Z_{Fe}-3)\cdot(N_{12}+N_{13}+N_{14}+2N_{15}+N_{16}+N_{17}) + (Z_{Ce}-4)\cdot(N_{18}+N_{19}+2N_{20}+2N_{21}+N_{22}+N_{23}+N_{24}) + (Z_{Ce}-3)\cdot(N_{25}+N_{26}+N_{27}+N_{28}+N_{29}) = (Z_{Fe}-2)\cdot N_{05} + (Z_{Ce}-4)\cdot N_{01}$ (14)

Applying the relations:

$[X_i^{z_i}]\cdot(V_0+V) = 10^3\cdot\frac{N_i}{N_A}$, $C_0V_0 = 10^3\cdot N_{01}/N_A$, and $CV = 10^3\cdot N_{05}/N_A$ (15)

in Eq. 14, we obtain the equation for GEB, written in terms of molar concentrations

$(Z_{Fe}-2)([Fe^{+2}]+[FeOH^{+1}]+[FeSO_4]) + (Z_{Fe}-3)([Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}] +[FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}]) + (Z_{Ce}-4)([Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] +[Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) + (Z_{Ce}-3)([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}])$
$= ((Z_{Fe}-2)\cdot C_0V_0 + (Z_{Ce}-4)\cdot CV)/(V_0+V)$ (14a)

Other linear combinations are also possible. Among others, we obtain the simpler form of GEB

$3f_5 + 3f_6 - (f_{12} + f_0 - 6f_3 - 4f_4) = 0$

$(N_{11}+N_{12}+N_{13}) - (N_{21}+N_{22}+2N_{23}+2N_{24}+N_{25}+N_{26}+N_{27}) = N_{01} - N_{05} \ \Rightarrow$ (16)

$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4] - ([Ce^{+4}]+[CeOH^{+3}]+2[Ce_2(OH)_3^{+5}]+2[Ce_2(OH)_4^{+4}]+ [CeSO_4^{+2}]+[Ce(SO_4)_2]+[Ce(SO_4)_3^{-2}]) = (C_0V_0 - CV)/(V_0+V)$ (16a)

From Eq. 11, considered as the *pr*imary form of Generalized Electron Balance (GEB), f_{12} = *pr*-GEB, we obtain the equation

$-[H^{+1}] + [OH^{-1}] + 7[HSO_4^{-1}] + 8[SO_4^{-2}] + 4[H_2CO_3] + 5[HCO_3^{-1}] + 6[CO_3^{-2}] + [FeOH^{+1}] + 8[FeSO_4] + [FeOH^{+2}] + 2[Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}]+8[FeSO_4^{+1}]+16[Fe(SO_4)_2^{-1}] + [CeOH^{+3}] + 3[Ce_2(OH)_3^{+5}] + 4[Ce_2(OH)_4^{+4}] + 8[CeSO_4^{+2}] + 16[Ce(SO_4)_2] + 24[Ce(SO_4)_3^{-2}] + [CeOH^{+2}] +$

$8[CeSO_4^{+1}] + 16[Ce(SO_4)_2^{-1}] + 24[Ce(SO_4)_3^{-3}] = (16CV + 6(C_{01}V_0 + C_1V) + 4(C_{02}V_0 + C_2V))/(V_0+V)$ (11a)

where, in addition to relations 15, we apply

$C_1V = 10^3\cdot\frac{N_{02}}{N_A}$, $C_{01}V_0 = 10^3\cdot\frac{N_{06}}{N_A}$, $C_2V = 10^3\cdot\frac{N_{04}}{N_A}$, $C_{02}V_0 = 10^3\cdot\frac{N_{08}}{N_A}$ (17)

From Eq. 13 we have

$2\cdot([Fe^{+2}]+[FeOH^{+1}]+[FeSO_4]) + 3\cdot([Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+ [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}]) + 4\cdot([Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) + 3\cdot([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}]) = (2\cdot C_0V_0 + 4\cdot CV)/(V_0+V)$ (13a)

As we see, the linear combination $f_{12} + f_0 - 6f_3 - 4f_4 = 0$ of balances for electron-non-active elements and f_0 = ChB, gives the Equations 13a and 14a, containing only the components and species, where electron-active elements (here: Fe, Ce) are involved. The coefficients/multipliers at the concentrations in Eq. 13a are equal to oxidation numbers of the corresponding components and species, with the electron-active elements involved.

The linear combination of Equations: 10 (multiplied by 2), 9 (multiplied by 4) and 13 givesthe shortest form of GEB

$[Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+[FeSO_4^{+1}]+[Fe(SO_4)_2^{-1}] - ([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}]) = 0$ (18)

where molar concentrations: C_0 and C are not involved explicitly. As we see, the shortest form, i.e., one composed of the smallest number of terms, is different from identity. In other words, the linear combinations are not reducible into identity, 0 = 0.

Equations 11a, 13a, 14a, 16a and 18, are equivalent to each other. All of them have full properties of the GEB, obtained according to Approach II to GEB. Other linear combinations of f_{12} with f_0, f_3,…,f_6 are also acceptable/possible, from algebraic viewpoint. In particular, Eq. 14a is identical with the one obtained according to Approach I to GEB, according to "card game" principle, described convincingly and illustrated artfully.

Briefly, according to Approach I to GEB, the common pool of electrons, introduced by Fe and Ce as the electron-active elements (players) (Michałowska-Kaczmarczyk et al., 2017), is $(Z_{Fe}-2)\cdot N_{01} + (Z_{Ce}-4)\cdot N_{05}$. These electrons are dissipated between different species formed by Fe and Ce in the mixture, namely: $(Z_{Fe}-2)N_9$of Fe-electrons in $Fe^{+2}\cdot n_9H_2O$, $(Z_{Fe}-2)N_{13}$ of Fe-electrons in $FeOH^{+1}\cdot n_{13}H_2O$, … , $(Z_{Ce}-4)N_{18}$of Ce-electrons in $Ce^{+4}\cdot n_{18}H_2O$, … , $2(Z_{Ce}-4)N_{20}$ of Ce-electrons in $Ce_2(OH)_3^{+5}\cdot n_{20}H_2O$, … , $(Z_{Ce}-3)N_{29}$ of Ce-electrons in $Ce(SO_4)_3^{-3}\cdot n_{29}H_2O$. Then the electron balance is presented by Eq. 26 and then by Eq. 26a. This way, the equivalency of Approaches I and II to GEB is proved.

For calculation purposes, the GEB, e.g. Eq. 18, is completed by charge and concentrations balances, obtained from Equations 6-10 and relations 15, 17:

$[H^{+1}] - [OH^{-1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] - [HCO_3^{-1}] - 2[CO_3^{-2}] + 2[Fe^{+2}] + [FeOH^{+1}] + 3[Fe^{+3}] + 2[FeOH^{+2}] + [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] - [Fe(SO_4)_2^{-1}] + 4[Ce^{+4}] + 3[CeOH^{+3}] + 5[Ce_2(OH)_3^{+5}] + 4[Ce_2(OH)_4^{+4}] + 2[CeSO_4^{+2}] - 2[Ce(SO_4)_3^{-2}] + 3[Ce^{+3}] + 2[CeOH^{+2}] + [CeSO_4^{+1}] - [Ce(SO_4)_2^{-1}] - 3[Ce(SO_4)_3^{-3}] = 0$ (6a)

$[HSO_4^{-1}] + [SO_4^{-2}] + [FeSO_4] + [FeSO_4^{+1}] + 2[Fe(SO_4)_2^{-1}] + [CeSO_4^{+2}] + 2[Ce(SO_4)_2] + 3[Ce(SO_4)_3^{-2}] + [CeSO_4^{+1}] + 2[Ce(SO_4)_2^{-1}] + 3[Ce(SO_4)_3^{-3}] - (C_0V_0 + C_{01}V_0 + 2CV + C_1V)/(V_0+V) = 0$ (7a)

$[H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] - (C_{02}V_0 + C_2V)/(V_0+V) = 0$ (8a)

$[Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}] + [Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}] - CV/(C_0+V) = 0$ (9a)

$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4] + [Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+[FeSO_4^{+1}]+[Fe(SO_4)_2^{-1}] - C_0V_0/(V_0+V) = 0$ (10a)

The set of independent equilibrium constants for this system is involved in relations:

$[H^{+1}][OH^{-1}] = 10^{-14.0}$; $[HSO_4^{-1}] = 10^{1.8}[H^{+1}][SO_4^{-2}]$; $[H_2CO_3] = 10^{16.4}[H^{+1}]^2[CO_3^{2}]$; $[HCO_3^{-1}] = 10^{10.1}[H^{+1}][CO_3^{-2}]$;

$[Fe^{+3}] = [Fe^{+2}]\cdot 10^{A(E - 0.771)}$; $[Ce^{+4}] = [Ce^{+3}]\cdot 10^{A(E-1.70)}$; $[FeOH^{+1}] = 10^{4.5}[Fe^{+2}][OH^{-1}]$;

$[FeOH^{+2}] = 10^{11.0}[Fe^{+3}][OH^{-1}]$; $[Fe(OH)_2^{+1}] = 10^{21.7}[Fe^{+3}][OH^{-1}]^2$; $[Fe_2(OH)_2^{+4}] = 10^{21.7}[Fe^{+3}]^2[OH^{-1}]^2$; $[FeSO_4] = 10^{2.3}[Fe^{+2}][SO_4^{-2}]$; $[FeSO_4^{+1}] = 10^{4.18}[Fe^{+3}][SO_4^{-2}]$; $[Fe(SO_4)_2^{-1}] = 10^{7.4}[Fe^{+3}][SO_4^{-2}]^2$; $[CeOH^{+2}] = 10^{5.0}[Ce^{+3}][OH^{-1}]$; $[CeOH^{+3}] = 10^{13.3}[Ce^{+4}][OH^{-1}]$; $[Ce_2(OH)_3^{+5}] = 10^{13.3}[Ce^{+4}]^2[OH^{-1}]^3$;

$[Ce_2(OH)_3^{+5}] = 10^{40.3}[Ce^{+4}]^2[OH^{-1}]^3$; $[Ce_2(OH)_4^{+4}] = 10^{53.7}[Ce^{+4}]^2[OH^{-1}]^4$; $[CeSO_4^{+1}] = 10^{1.63}[Ce^{+3}][SO_4^{-2}]$;

$[Ce(SO_4)_2^{-1}] = 10^{2.34}[Ce^{+3}][SO_4^{-2}]^2$; $[Ce(SO_4)_3^{-3}] = 10^{3.08}[Ce^{+3}][SO_4^{-2}]^3$; $[CeSO_4^{+2}] = 10^{3.5}[Ce^{+4}][SO_4^{-2}]$; $[Ce(SO_4)_2] = 10^{8.0}[Ce^{+4}][SO_4^{-2}]^2$; $[Ce(SO_4)_3^{-2}] = 10^{10.4}[Ce^{+4}][SO_4^{-2}]^3$ (19)

In this case, the number K=6 of the basic/independent variables x_k is equal to the number of balances, see Equations 6a – 10a and e.g. Eq. 18,where

$\mathbf{x} = [x_1,\ldots,x_6]^T = [E, pH, pCe3, pFe2, pSO4, pH2CO3]^T$ (20)

Potential E, pH = –log[H^{+1}], pCe3 = –log[Ce^{+3}], pFe2 = –log[Fe^{+2}], pSO4 = –log[SO_4^{-2}], pH2CO3 = –log[H_2CO_3] are defined for particular V values of the titrant added.

The individual 'homogeneous' variables (20) appear in the exponents of the power of 10, namely

$[e^{-1}] = 10^{-A\cdot E}$, $[H^{+1}] = 10^{-pH}$, $[Ce^{+3}] = 10^{-pCe3}$, $[Fe^{+2}] = 10^{-pFe2}$, $[SO_4^{-2}] = 10^{-pSO4}$, $[H_2CO_3] = 10^{-pH2CO3}$ (21)

where

A = F/(R*T*·ln10) = 16.9 for *T* = 298 K.

The equations (6a) - (10a), (18) and relations (19) for equilibrium constants form an algorithm involved in the iterative computer program, e.g. MATLAB.

Simulated titration curves

Fraction titrated

The results of simulated titrations in the D+T system considered can be represented graphically by plots of the relationships: with measurable quantities: potential E and pH on the ordinate and volume V of the titrant (T) added on the abscissa. In this case, it is more advantageous/reasonable to plot the graphs:E = E(Φ), pH = pH(Φ)with the fraction titrated [29]

$$\Phi = \frac{C\cdot V}{C_0\cdot V_0} \quad (22)$$

on the abscissa, where C_0 – concentration [mol/L] of the analyte A =$FeSO_4$in D, C – concentration [mol/L] of the reagent B = $Ce(SO_4)_2$in T; it provides a kind of uniformity/normalization of the related plots. Moreover, the speciation curves $\log[X_i^{z_i}] = \Theta_i(\Phi)$ can also be plotted for different species $X_i^{z_i}\cdot n_{iW}$. The corresponding relationships can also be presented in a tabulated form. These data can be then used in the context of an analysis error considered from the viewpoint of Generalized Equivalence Mass (GEM) (Meija et al., 2017).

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. 22) assumes the value

$$\Phi_{eq} = \frac{C\cdot V_{eq}}{C_0\cdot V_0} \quad (23)$$

In contradistinction to visual titrations, where the end volume $V_e \cong V_{eq}$ is registered, see e.g. [29], all instrumental titrations aim, in principle, to obtain the V_{eq} value on the basis of experimental data {(V_j, y_j) | j=1,…,N}, where y = pH or E for potentiometric methods of analysis. Referring again to Eq. 22, we have

$$C_0\cdot V_0 = 10^3\cdot\frac{m_A}{M_A} \quad (24)$$

where m_A [g] and M_A [g/mol] denote mass and molar mass of analyte (A), respectively. From Equations: 22 and 24, we get

$$m_A = 10^{-3}\cdot C\cdot M_A\cdot\frac{V}{\Phi} \quad (25)$$

The value of the fraction $\frac{V}{\Phi}$in Eq. 25, obtained from Eq. 22,

$$\frac{V}{\Phi} = \frac{C_0\cdot V_0}{C} \quad (26)$$

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

$$\frac{V}{\Phi} = \frac{V_e}{\Phi_e} = \frac{V_{eq}}{\Phi_{eq}} \quad (27)$$

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

$$\Phi_e = \frac{C\cdot V_e}{C_0\cdot V_0} \quad (28)$$

is the Φ-value related to the end point. From Equations 25 and 27, one obtains:

$$\text{(a) } m_A = 10^{-3}\cdot C\cdot V_e\cdot\frac{M_A}{\Phi_e} \quad \text{and} \quad \text{(b) } m_A = 10^{-3}\cdot C\cdot V_{eq}\cdot\frac{M_A}{\Phi_{eq}} \quad (29)$$

This does not mean that we may choose between Equations 29a and 29b, to calculate m_A. Namely, Eq. 29a 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. 29b 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 the Equations: 29a and 29b appear to be useless, the third, approximate formula for m_A, has to be applied Michałowska-Kaczmarczyk and Michałowski, 2018), namely:

$$m'_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_{eq}} \quad \Rightarrow \quad m'_A = 10^{-3} \cdot C \cdot V_e \cdot R_A^{eq} \qquad (30)$$

where Φ_{eq} is put for Φ_e in Eq. 29a, and

$$R_A^{eq} = \frac{M_A}{\Phi_{eq}} \qquad (31)$$

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

$$\delta = \frac{m'_A - m_A}{m_A} = \frac{m'_A}{m_A} - 1 = \frac{V_e}{V_{eq}} - 1 = \frac{\Phi_e}{\Phi_{eq}} - 1 \quad (32)$$

The Generalized Equivalence Mass (GEM) was formulated (1979) by Michałowski, as the counterproposal to earlier (1978) IUPAC decision, see (Ponikvar et al., 2008).

Graphical presentation of results obtained from calculations

The results of calculations obtained for simulated titration of V_0 = 100 mL of $FeSO_4$ (C_0 = 0.01 mol/L) + H_2SO_4 (C_{01}) as D titrated with V mL of $Ce(SO_4)_2$ (C = 0.1 mol/L) + H_2SO_4 (C_1 = 0.5 mol/L) as T are presented in Figures 1 - 4; different C_{01} values and $C_{02} = C_2 = 0$ were assumed there.

The changes in shape of the curves E = E(Φ) and pH = pH(Φ), detailed in Figures 2a,b and 3, resulted mainly from differences between C_{01} and C_1 values. Note that the solution of $Ce(SO_4)_2$ is prepared by dissolution of this salt in H_2SO_4. The plot obtained at $C_{01} = C_1 = 0.5$ is not exactly parallel to Φ-axis (Fig. 3); small changes in pH value result there from dilution and complexation effects (different for Ce and Fe species).

Some remarks

1. *Concerns cores, fans and players*. Cores are composed of fans, within the species containing also other fans or players. In the system considered here, SO_4^{-2} is the core (composed of O and S as fans) that enters the species: $HSO_4^{-1} \cdot n_4H_2O$, $SO_4^{-2} \cdot n_5H_2O$, $FeSO_4 \cdot n_{11}H_2O$, $FeSO_4^{+1} \cdot n_{16}H_2O$, $Fe(SO_4)_2^{-1} \cdot n_{17}H_2O$, $CeSO_4^{+2} \cdot n_{22}H_2O$, $Ce(SO_4)_2 \cdot n_{23}H_2O$, $Ce(SO_4)_3^{-2} \cdot n_{24}H_2O$, $CeSO_4^{+1} \cdot n_{27}H_2O$, $Ce(SO_4)_2^{-1} \cdot n_{28}H_2O$, $Ce(SO_4)_3^{-3} \cdot n_{29}H_2O$.

where H, O, S are fans, and Fe and Ce are players. The players are interrelated in the relations:

$[Fe^{+3}] = [Fe^{+2}] \cdot 10^{A(E - 0.771)}$; $[Ce^{+4}] = [Ce^{+3}] \cdot 10^{A(E - 1.70)}$,

where potential E is involved.

2. *Concerns* f_{12}. When formulating the balances f_1 and f_2, it can also be assumed that some water molecules are bound in clusters $(H_2O)_\lambda$ ($N_{1,\lambda}$, λ =1, 2,...) in aqueous solutions [43]. Writing these balances as follows:

$f_1 = f(H)$:

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

$f_2 = f(O)$:

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

we have:

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

$- N_2 + N_3 + ...$

i.e., all components related to the clusters are cancelled.

Final Comments

Physical theories reconstruct the properties and behavior of Nature in mathematical mode. The comparison of some predictions of basic physical theories with empirical data indicates that this reconstruction is extremely (sometimes - unimaginably) accurate.

The correct thermodynamic approach to the problem within GATES/GEB is based on a solution of a system of algebraic equations, not on a (pre-assumed) chemical reaction notation, as were done previously/elsewhere. The formulation of reaction notations on the basis of the related speciation plots is a next, facultative (notobligatory) step made after calculations made according to GATES/GEB principles and graphical presentation of the results thus obtained.

The GEB is the hidden connection of physicochemical laws, and the breakthrough in thermodynamic theory of electrolytic redox systems. The GEB, considered as the general Law of Nature, provides the real proof of the Harmony in Nature. Paraphrasing a Chinese proverb, one can figuratively say that "the lotus flower, lotus leaf and lotus seed come from the same root" (Toporek et al., 2015). Similarly, the three kinds of balances: GEB, charge and elemental/core balances come from the same family of fundamental laws of preservation.

All the inferences made within GATES/GEB are based on firm, mathematical (algebraic) foundations, not on an extremely "fragile" chemical notation principle that is only a faint imitation of a true, algebraic notation, as indicated in the series of our review papers cited above. The approach proposed allows to understand far better all physicochemical phenomena occurring in the system in question and improve some methods of analysis. All the facts testify very well about the potency of simulated calculations made, according to GATES, on the basis of all attainable physicochemical knowledge. In this context GATES/GEBdeserves a due attention and promotion among physicochemists and chemists–analysts, as the best thermodynamic approach to electrolytic redox systems.

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