

## Research Article

# The Importance of Linear Combinations in Theory of Electrolytic Systems

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## Abstract

The fundamental property of any electrolytic system (aqueous media), involved with the linear combination  $f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(\text{O}) - f(\text{H})$  of elemental balances:  $f_1 = f(\text{H})$  for hydrogen (H) and  $f_2 = f(\text{O})$  for oxygen (O), related to redox and non-redox systems, is presented as the hidden connection of physicochemical laws, and as the breakthrough in thermodynamic theory of electrolytic redox systems. When combined with charge balance ( $f_0 = \text{ChB}$ ) and elemental/core balances  $f_k = f(\text{Y}_k)$  ( $k=3, \dots, K$ ) for elements/cores  $\text{Y}_k \neq \text{H}, \text{O}$ , the  $f_{12}$  provides a criterion distinguishing between non-redox and redox systems. The criterion of linear independency or dependency of the equations  $f_0, f_{12}, f_3, \dots, f_k$  is the conclusion resulting from algebraic properties of the balances  $f_0, f_1, f_2, f_3, \dots, f_k$  formulated for redox and non-redox electrolytic systems. The supreme role of this criterion in relation to the oxidation number (ON), perceived hitherto in chemistry as the contractual concept, will be proved herein on the example of cerimetric titration of ferrous ions, realized according to potentiometric mode. Thus the chapter concerns very fundamental (but unknown in earlier literature) regularities obligatory for electrolytic systems, of different complexity. The 'rules' involved with controversial assumptions related hitherto to ON's, may find here a logical, more convincing justification.

**Keywords:** Electrolytic Redox Systems; GATES/GEB; Approach I to GEB; Approach II to GEB; Oxidation numbers.

## Introduction

The quantitative, thermodynamic description of any electrolytic system requires prior information on: (1<sup>o</sup>) the detailed knowledge of species present in the system considered; (2<sup>o</sup>) the equilibrium constants; (3<sup>o</sup>) the balances. The balances and expressions for equilibrium constants interrelate molar concentrations of some species in the system. To do it, we should necessarily define these terms in an unambiguous manner. This possibility is provided by the Generalized Approach to Electrolytic Systems (GATES) [1-35] which offers the best tool applicable for thermodynamic resolution of electrolytic systems, of any degree of complexity.

All these general remarks/requirements, related to GATES and GATES/GEB in particular, are referenced to electrolytic systems (aqueous, non-aqueous or mixed-solvent media), where the balances expressing the laws of charge and elements conservation in closed systems are formulated and interrelated in accordance with the principles of linear combination, known in elementary algebra. Within GATES, the charge and elements conservation laws are related to all components/species of the electrolytic system. On this basis, the Generalized Electron Balance (GEB) concept, perceived as a law of Nature, is derived. The linear combinations of the balances provide the criterion distinguishing between non-redox and redox systems, and the Generalized Electron Balance (GEB), perceived as a law of Nature, as the equation needed/indispensable for resolution of redox systems, as a hidden connection of physicochemical laws. The multipliers applied purposely in linear combinations of equations/balances related to redox and non-redox systems provide

the values of oxidation numbers (ON's). The discussion on the linear independency/dependency property of the balances will be preceded by simple example, known from elementary algebra course.

## Linear Dependence of Algebraic Equations

The principle of linear combination of algebraic equations plays a fundamental/decisive role in thermodynamics of electrolytic systems, considered according to the GATES principles. We refer here to the problem of linear dependency of balances – analogous to the problem of dependency of linear equations, considered in elementary algebra. In this context, the general property of linear independency, inherently involved with redox systems, will be emphasized.

For the beginning, let us take the set of linear equations [27]:

$$a_{11}x_1 + a_{12}x_2 + a_{13}x_3 = b_1$$

$$a_{21}x_1 + a_{22}x_2 + a_{23}x_3 = b_2$$

Completed by linear combination of these equations, i.e.,

$$c_1(a_{11}x_1 + a_{12}x_2 + a_{13}x_3) + c_2(a_{21}x_1 + a_{22}x_2 + a_{23}x_3) \equiv (c_1a_{11} + c_2a_{21})x_1 + (c_1a_{12} + c_2a_{22})x_2 + (c_1a_{13} + c_2a_{23})x_3 = c_1b_1 + c_2b_2$$

Applying the matrix algebra, we see that the determinant

$$D = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ c_1 \cdot a_{11} + c_2 \cdot a_{21} & c_1 \cdot a_{12} + c_2 \cdot a_{22} & c_1 \cdot a_{13} + c_2 \cdot a_{23} \end{vmatrix}$$

has zero value

$$\mathcal{D} = C_1 \cdot \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{11} & a_{12} & a_{13} \end{vmatrix} + C_2 \cdot \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{21} & a_{22} & a_{23} \end{vmatrix} = C_1 \cdot 0 + C_2 \cdot 0$$

irrespectively on the  $c_1$  and  $c_2$  values; at  $\mathcal{D} = 0$ , calculation of  $x_1$ ,  $x_2$  and  $x_3$  is then impossible.

Checking the linear dependency or independency of linear algebraic equations is, in general case, a very burdensome and time-consuming task/activity, susceptible to simple mistakes, see comments in [31]. However, it turns out that the simple method of transformation of a linear combination of equations to the identity,  $0 = 0$ , is extremely effective, even in reference to complicated electrolytic systems. The rules involved with formulation of these combinations will be presented /exemplified in further sections of this chapter.

## Components and Species

The terms: components of the system and species in the system are distinguished. After mixing the components, a mixture of defined species is formed. We refer here to aqueous electrolytic systems, where the species  $X_i^{z_i}$  exist as hydrates  $X_i^{z_i} \cdot n_{iW}$ ,  $i=1, \dots, I$ ;  $z_i = 0, \pm 1, \pm 2, \dots$  is a charge, expressed in elementary charge units,  $e = F/N_A$  ( $F = 96485.333 \text{ C} \cdot \text{mol}^{-1}$  – Faraday’s constant,  $N_A = 6.022141 \cdot 10^{23} \text{ mol}^{-1}$  – Avogadro’s number);  $n_i = n_{iW} = n_i \text{H}_2\text{O} \geq 0$  is a mean number of water ( $W = \text{H}_2\text{O}$ ) molecules attached to  $X_i^{z_i}$ ; the case  $n_{iW} = 0$  is then also admitted. Thus the components form a (sub) system, and the species  $X_i^{z_i} \cdot n_{iW}$  enter the system thus formed.

For some reasons, it is justifiable to start the balancing from the numbers of particular entities:  $N_{0j}$  – for components ( $j = 1, \dots, J$ ) represented by molecules, and  $N_i$  – for species (ions and molecules) of  $i$ -th kind ( $i = 1, \dots, I$ ), where  $I$  is the number of kinds of the species. The mono- or two-phase electrolytic system thus obtained involve  $N_i$  molecules of  $\text{H}_2\text{O}$  and  $N_i$  species of  $i$ -th kind,  $X_i^{z_i} \cdot n_{iW}$  ( $i=2, 3, \dots, I$ ), specified briefly as  $X_i^{z_i} (N_i, n_i)$ , where  $n_i \equiv n_{iW} \equiv n_i \text{H}_2\text{O}$ . For ordering purposes, we write:  $\text{H}^+ (N_2, n_2)$ ,  $\text{OH}^- (N_3, n_3), \dots$ , i.e.,  $z_2 = 1, z_3 = -1, \dots$ . The  $X_i^{z_i}$ s, with different numbers of  $\text{H}_2\text{O}$  molecules involved in  $X_i^{z_i} \cdot n_{iW}$ , e.g.  $\text{H}^+$ ,  $\text{H}_3\text{O}^{+1}$  and  $\text{H}_9\text{O}_4^{+1}$ ;  $\text{H}_4\text{IO}_6^{-1}$  and  $\text{IO}_4^{-1}$ , are considered equivalently, i.e., as the same species in this medium. The  $n_i = n_{iW} = n_i \text{H}_2\text{O}$  values are virtually unknown – even for  $X_2^{z_2} = \text{H}^+$  [36] in aqueous media, and depend on ionic strength ( $I$ ) of the solution.

The notation  $X_i^{z_i} \cdot n_{iW}$ ,  $W$  for the species will be practiced on the step of formulation of the related balances; this viewpoint has several advantages. First, it presents the species in natural forms in aqueous media. This way, after linear combinations of the related balances, one can discover some regularity hidden earlier by notation of the species in the form  $X_i^{z_i}$ . This notation can be extended on electrolytic systems in mixed-solvent  $A_s (s=1, \dots, S)$  media, where mixed solvates  $X_i^{z_i} \cdot n_{iA_1} \dots n_{iA_s}$  are assumed, and  $n_{iA_s} \geq 0$  is the mean numbers of  $A_s (s=1, \dots, S)$  molecules attached to  $X_i^{z_i}$  [32-35]. In other instances, the common/simpler notation  $X_i^{z_i}$  of the species, e.g.  $\text{HSO}_4^{-1} \cdot n_5 \text{H}_2\text{O}$  as  $\text{HSO}_4^{-1}$ , will be practiced. Molar concentrations [mol/L] of the species are denoted as  $[X_i^{z_i}]$ , for brevity. All concentrations of components and species are expressed in mol/L, and all volumes – in mL.

Any electrolytic system can be perceived as a macroscopic part of the universe selected for observation and experimentation. For

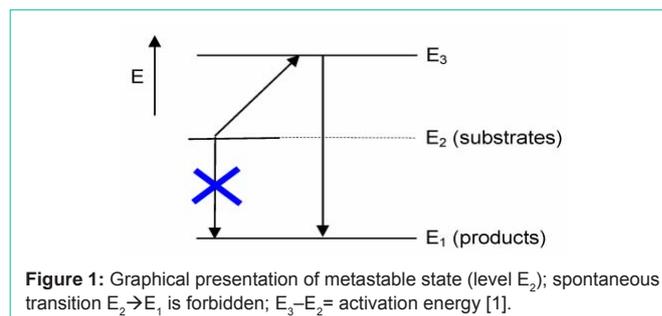


Figure 1: Graphical presentation of metastable state (level  $E_2$ ); spontaneous transition  $E_2 \rightarrow E_1$  is forbidden;  $E_3 - E_2 =$  activation energy [1].

modelling purposes, the concept of a closed system:

$$\text{matter} \not\leftrightarrow \text{system/subsystems} \leftrightarrow \text{heat}$$

Separated from the environment (surroundings) by diathermal (freely permeable by heat) walls as boundaries, is assumed in GATES. Diathermal walls are impermeable ( $\not\leftrightarrow$ ) to matter ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{O}_2, \dots$ ), but permeable ( $\leftrightarrow$ ) to heat. Thus the diathermal walls allow the heat exchange between the (sub) system(s), and the environment. The temperature changes, resulting from exo- or endothermic effects occurred in the system may influence the equilibrium constants values. Constant temperature ( $T = \text{const.}$ ) is one of the conditions securing constancy of equilibrium constants values. Any chemical process, such as titration, with titrand  $D$  and titrant  $T$  as subsystems composing the  $D+T$  system, is carried out under isothermal conditions, in a quasi-static manner.

## Notation of Balances

In aqueous media, we formulate charge balance  $f_0 = \text{ChB}$  and elemental balances:  $f_1 = f(\text{H})$  for  $E_1 = \text{H}$  (hydrogen) and  $f_2 = f(\text{O})$  for  $E_2 = \text{O}$  (oxygen),... Other elemental or core balances will be denoted as  $f_k = f(Y_k)$ ,  $Y_k = E_k$  or  $\text{core}_k$  ( $k=3, \dots, K$ ). 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 [27]. For example,  $\text{SO}_4^{-2}$  is a core within sulphate species:  $\text{HSO}_4^{-1} \cdot n_4 \text{H}_2\text{O}$ ,  $\text{SO}_4^{-2} \cdot n_5 \text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot n_{11} \text{H}_2\text{O}$  in the  $D$  subsystem considered in section 6.1.2.

In order to formulate the reliable (formally correct) balances for a given system, it is necessary to collect detailed, possibly complete (qualitative and quantitative) information regarding this system. The qualitative information concerns the components that make up the given system, and the species formed in this system. This information should subject thorough verification, for example regarding the preparation of the appropriate solutions; e.g.  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  is dissolved in  $\text{H}_2\text{SO}_4$  solution, not in pure, distilled water, to avoid precipitation of cerium hydroxide. The collection of information about species formed in the system requires more effort. The sources of information are here tables with appropriate physicochemical constants, such as dissociation constants of weak acids, stability constants of complexes, solubility products, etc. These constants interrelate concentrations of complex species with concentrations of their composing, simpler forms, involved in stoichiometric reaction, e.g.,  $\text{HSO}_4^{-1} = \text{H}^+ + \text{SO}_4^{-2}$ ;  $\text{Fe}^{+3} + 2\text{SO}_4^{-2} = \text{Fe}(\text{SO}_4)_2^{-1}$ .

In quantitative description of redox systems, the standard potentials  $E_{0i}$  are also applied. The  $E_{0i}$  interrelate concentrations of the species with different oxidation degrees of a given element, involved

in the related stoichiometric reaction, e.g.,  $\text{Fe}^{+3} + \text{e}^{-1} = \text{Fe}^{+2}, \text{Ce}^{+4} + \text{e}^{-1} = \text{Ce}^{+3}$ . All the equilibrium constants were determined experimentally, and hence subjected to errors of various kind, as discussed e.g. in [35]. Nevertheless, despite these objections, the basic requirements must be met, namely: the set of these constants should be complete and consistent [27].

The components and species of redox systems are involved in GEB, charge (ChB), and concentration balances, and in a set of expressions for equilibrium constants. However, it should be noted that certain components (or groups of components) remain at metastable state with respect to each other, e.g. (1)  $\text{KMnO}_4$  and  $\text{H}_2\text{O}$  [1], or (2)  $\text{H}_2\text{S}$  and  $\text{H}_2\text{SO}_4$  [37], at room temperature. And so,  $\text{KMnO}_4$  does not oxidize  $\text{H}_2\text{O}$ , i.e., none products of  $\text{H}_2\text{O}$  oxidation are formed in the system. Also none products of sulphur symproportionation are produced in the system formed from a mixture of diluted  $\text{H}_2\text{S}$  and  $\text{H}_2\text{SO}_4$  solutions. On the other hand, in computer programs one can run some reaction paths to check “what would happen” if such reaction products were created in a metastable system [1]. In these cases, one can compare the course/changes of the relevant measurands, e.g. pH and/or potential E, in a simulated titration procedure implemented in computer program, and in the experimental titration. In some cases, at the stage of collecting the relevant physicochemical data, one may have the impression of a lack of knowledge regarding the putative components in the respective systems. In any case, the putative components may be included in the respective balances, together with the corresponding equilibrium constants, pre-assumed arbitrarily. The dependences for measurable quantities obtained here can be then compared with the data obtained experimentally. On a similar principle, the simulated curves obtained after applying equilibrium data obtained from various sources (tables of equilibrium data) can be compared with each other, and with experimental results. On this simple way, one can get a lot of thermodynamic information about the system tested. Undoubtedly, this ‘theme and variations’ requires a kind of intellectual activity.

### Titrand, Titrant and Titration

Static and dynamic systems, with water as the main component/solvent, are considered below. A static system is obtained by disposable mixing different components as solutes with water. In particular, titrant T and titrand D can be perceived as static subsystems of the dynamic D+T system, realized during the titration  $\text{T}(\text{V}) \Rightarrow \text{D}(\text{V}_0)$ , where – at defined point of the titration – V mL of T is added into  $\text{V}_0$  mL of D and  $\text{V}_0 + \text{V}$  mL of D+T system/mixture is thus obtained, if the assumption of additivity in the volumes is valid/tolerable. In general, D and T are composed of one or more solutes dissolved in water.

Note that the concentrations: C,  $C_p$ ,  $C_o$ ,  $C_{o1}$  of the related components (in T and D) are intensive parameters.

The results of titrations, with pH and/or potential E of D+T system registered, are plotted as functions of volume V of the titrant (T) added, i.e.,  $\text{pH} = \text{pH}(\text{V})$ ,  $\text{E} = \text{E}(\text{V})$ . In typical cases, it is advantageous/possible to plot the graphs:  $\text{E} = \text{E}(\Phi)$  (Figure 1a),  $\text{pH} = \text{pH}(\Phi)$  (Figure 2),  $\log[X_i^{z_i}]$  vs.  $\Phi$ , where

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \tag{1}$$

is the fraction titrated [1,8,9,38], and  $C_0$  – concentration [mol/L] of analyte A in D, C – concentration [mol/L] of reagent B in T; it

provides a kind of uniformity of the related plots. Namely, the use of  $\Phi$  on the abscissa allows to present, in normalized scale, the graphs with pH, E,  $\log[X_i^{z_i}]$  on the ordinate.

It is justifiable to start the quantitative considerations from the numbers of particular entities:  $N_{0j}$  – for components ( $j = 1, \dots, I$ ) represented by molecules, and  $N_i$  – for species (ions and molecules) of i-th kind ( $i = 1, \dots, I$ ), where I is the number of kinds of the species. The mono- or two-phase electrolytic system thus obtained involves  $N_1$  molecules of  $\text{H}_2\text{O}$  and  $N_i$  species of i-th kind,  $X_i^{z_i} \cdot n_{iw}$  ( $i=2, 3, \dots, I$ ), specified briefly as  $X_i^{z_i}(N_i, n_i)$ , where  $n_i \equiv n_{iw} \equiv n_i \text{H}_2\text{O}$ . For ordering purposes, we write:  $\text{H}^{+1}(N_2, n_2)$ ,  $\text{OH}^{-1}(N_3, n_3), \dots$ , i.e.,  $z_2 = 1, z_3 = -1, \dots$ . The net charge of  $X_i^{z_i} \cdot n_{iw}$  equals to the charge of  $X_i^{z_i} : z_i + n_{iw} \cdot 0 = z_i$ . The charge of a species  $X_i^{z_i} \cdot n_{iw}$ , expressed in elementary charge units, results from the numbers of protons in nuclei, and orbital electrons in atoms composing the species [8].

The notation  $X_i^{z_i} \cdot n_{iw}$  for the species is useful on the step of formulation of the related balances. This viewpoint has several advantages. First, it presents the species in natural forms in aqueous media. This way, after linear combinations of the related balances, one can discover some regularity hidden earlier by notation of the species in the form  $X_i^{z_i}$ . This notation can be extended on electrolytic systems in mixed-solvent  $A_s$  ( $s=1, \dots, S$ ) media, where mixed solvates  $X_i^{z_i} \cdot n_{iA_1} \dots n_{iA_s}$  are assumed, and  $n_{iA_s} \geq 0$  is the mean numbers of  $A_s$  ( $s=1, \dots, S$ ) molecules attached to  $X_i^{z_i}$  [32-34]. In other instances, the common/simpler notation  $X_i^{z_i}$  of the species, e.g.,  $\text{HSO}_4^{-1} \cdot n_4 \text{H}_2\text{O}$  as  $\text{HSO}_4^{-1}$ , will be practiced. Molar concentrations [mol/L] of the species are denoted as  $[X_i^{z_i}]$ , for brevity. All concentrations of components and species are expressed in mol/L, and all volumes – in mL.

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

$$f_0 = \sum_{i=2}^I z_i \cdot N_i = 0 \Rightarrow \sum_{i=2}^I z_i \cdot [X_i^{z_i}] = 0 \tag{2}$$

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

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

$$f_1 = f(\text{H}) = 2N_1 + \sum_{i=2}^I (a_{1i} + 2n_{iw}) \cdot N_i - \sum_{j=1}^J b_{1j} \cdot N_{0j} = 0 \tag{3}$$

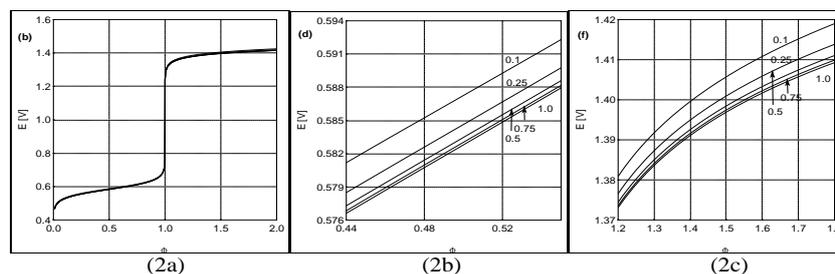
$$f_1 = f(\text{H}) = 2N_1 + \sum_{i=2}^I (a_{1i} + 2n_{iw}) \cdot N_i - \sum_{j=1}^J b_{1j} \cdot N_{0j} = 0 \tag{4}$$

Then the balance

$$f_2 = f(\text{O}) = N_1 + \sum_{i=2}^I (a_{2i} + n_{iw}) \cdot N_i - \sum_{j=1}^J b_{2j} \cdot N_{0j} = 0 \tag{5}$$

is formulated.

The elemental/core balances:  $f_3, \dots, f_k$  interrelating the numbers of atoms/cores  $Y_k \neq \text{H}, \text{O}$  in components and species, are as follows



**Figure 2:** The  $E = E(\Phi)$  curves plotted for the D+T system, at  $V_0 = 100$ ,  $C_0 = 0.01$ ,  $C = 0.1$ ,  $C_1 = 0.5$  and different  $C_{01}$  values, indicated at their enlarged fragments (b) at  $\Phi < \Phi_{eq}$ , (c) at  $\Phi > \Phi_{eq}$ .

$$f_k = f(Y_k) = \sum_{i=1}^I a_{ki} \cdot N_i - \sum_{j=1}^J b_{kj} \cdot N_{0j} = 0 \quad (k=3, \dots, K) \quad (6)$$

where  $a_{ki}$  and  $b_{kj}$  are the numbers of elements/cores  $Y_k$  in  $X_i^{Z_i} \cdot n_{iw}$ , and in the  $j$ -th component of the system, resp. 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; e.g.,  $SO_4^{2-}$  is a core within sulphate species:  $HSO_4^{-1} \cdot n_4 H_2O$ ,  $SO_4^{-2} \cdot n_5 H_2O$ ,  $FeSO_4 \cdot n_4 H_2O$  and  $FeSO_4 \cdot 7H_2O$  as component in the D subsystem (section 6.1.2). For example,  $N_4$  species  $HSO_4^{-1} \cdot n_4 H_2O$  involve  $N_4(1+2n_4)$  atoms of H (where  $a_{12}=1$ ),  $N_4(4+n_4)$  atoms of O (where  $a_{22}=4$ ), and  $N_4$  atoms of S;  $N_{05}$  molecules of  $FeSO_4 \cdot 7H_2O$  as a component involve  $14N_{05}$  atoms of H,  $11N_{05}$  atoms of O,  $N_{05}$  atoms of S and  $N_{05}$  atoms of Fe, i.e.,  $b_{15}=14$ ,  $b_{25}=11$ ,  $b_{35}=1$ ,  $b_{55}=1$ .

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

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

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

for elements with negative oxidation numbers, or

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

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.

The linear combination

$$f_0 + f_{12} - \sum_{k=3}^K d_k \cdot f_k = 0 \Leftrightarrow \sum_{k=3}^K d_k \cdot f_k - f_{12} - f_0 = 0 \Leftrightarrow$$

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

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

related linear combination (Eq. 7), as will be explained in examples presented below.

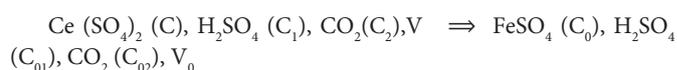
In Eq. 5 and then in Eq. 7, the terms involved with water, i.e.,  $N_{12}, N_{0j}$  (for  $j$  related to  $H_2O$  as the component), and  $n_i = n_{iW}$  are not involved. The necessity of prior knowledge of  $n_{iW}$  values in the balancing is thus avoided, already at the stage of  $f_{12}$  formulation.

Consequently, the set of  $K$  independent balances:  $f_0, f_{12}, f_3, \dots, f_K$  is related to a redox system, whereas  $f_0, f_3, \dots, f_K$  form the set of  $K-1$  independent balances related to a non-redox system, where  $f_3, \dots, f_K$  is the set of  $K-2$  elemental/core balances  $f_k = f(Y_k)$  for  $k=3, \dots, K$ , i.e., for  $Y_k \neq H, O$  (Eq. 6).

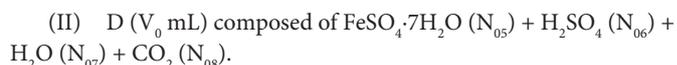
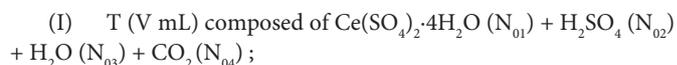
The balancing is necessary for computer simulation of titrimetric procedure according to GATES principles. Any titration is considered as a kind of dynamic process, where  $V$  mL of a titrant (T) is added into  $V_0$  mL of titrand (solution titrated, D);  $V$  is considered here as the steering variable. In graphical presentation of the data obtained from calculations, it is advisable to apply, on the abscissa, the values of fraction titrated  $\Phi$  (Eq. 1); it provides a kind of uniformity of the related plots.

## Modelling of Iron Cerimetric Titration

Let us refer to the titration  $T(V) \Rightarrow D(V_0)$ :

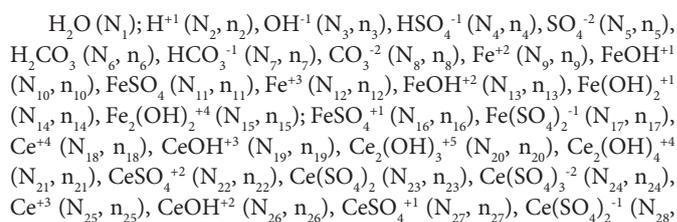


We consider here non-redox subsystems:



and

(III) D+T redox system as the mixture formed from T and D; the following species are formed/present there:



$$n_{28}), \text{Ce}(\text{SO}_4)_3^{-3} (N_{29}, n_{29}) \quad (8)$$

For example, the notation  $\text{HSO}_4^{-1} (N_4, n_4)$  applied here refers to  $N_4$  ions of  $\text{HSO}_4^{-1} \cdot n_4 \text{H}_2\text{O}$  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  $\text{CO}_2$  in T and D is considered here as an admixture from air, to approximate real conditions of the analysis, on the step of preparation of D and T; the titration  $\text{T(V)} \Rightarrow \text{D(V}_0)$  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 and different forms of GEB, resulting from linear combinations of charge and elemental balances related to D+T system, will be obtained. To avoid (possible) disturbances, the common notation (subscripts) assumed in the set (8) of species will be applied for components and species in T, D and D+T. In context with the dynamic D+T system, T and D are considered as static (sub) systems.

### Linear combination of balances

#### The T subsystem

We get here the balances:

$$\begin{aligned} f_0 &= \text{ChB} \\ N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 4N_{18} + 3N_{19} + 5N_{20} + 4N_{21} + 2N_{22} - 2N_{24} &= 0 \\ f_1 &= f(\text{H}) \\ 2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_{18}n_{18} + N_{19}(1+2n_{19}) + N_{20}(3+2n_{20}) + N_{21}(4+2n_{21}) + 2N_{22}n_{22} + 2N_{23}n_{23} + 2N_{24}n_{24} &= 8N_{01} + 2N_{02} + 2N_{03} \\ f_2 &= f(\text{O}) \\ N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_{18}n_{18} + N_{19}(1+n_{19}) + N_{20}(3+n_{20}) + N_{21}(4+n_{21}) + N_{22}(4+n_{22}) + N_{23}(8+n_{23}) + N_{24}(12+n_{24}) &= 12N_{01} + 4N_{02} + N_{03} + 2N_{04} \\ -f_3 &= -f(\text{SO}_4) \\ 2N_{01} + N_{02} &= N_4 + N_5 + N_{22} + 2N_{23} + 3N_{24} \\ -f_4 &= -f(\text{CO}_3) \\ N_{04} &= N_6 + N_7 + N_8 \\ -f_5 &= -f(\text{Ce}) \\ N_{01} &= N_{18} + N_{19} + 2N_{20} + 2N_{21} + N_{22} + N_{23} + N_{24} \\ f_{12} &= 2 \cdot f_2 - f_1 \\ -N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{19} + 3N_{20} + 4N_{21} + 8N_{22} + 16N_{23} + 24N_{24} &= 16N_{01} + 6N_{02} + 4N_{04} \end{aligned}$$

The linear combination

$$f_{12} + f_0 - 6 \cdot f_3 - 4 \cdot f_4 - 4 \cdot f_5 = 0 \quad (9)$$

as the simple sum of collected balances:

$$\begin{aligned} -N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{19} + 3N_{20} + 4N_{21} + 8N_{22} + 16N_{23} + 24N_{24} &= 16N_{01} + 6N_{02} + 4N_{04} \\ N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 4N_{18} + 3N_{19} + 5N_{20} + 4N_{21} + 2N_{22} - 2N_{24} &= 0 \\ 12N_{01} + 6N_{02} &= 6N_4 + 6N_5 + 6N_{22} + 12N_{23} + 18N_{24} \\ 4N_{04} &= 4N_6 + 4N_7 + 4N_8 \\ 4N_{01} &= 4N_{18} + 4N_{19} + 8N_{20} + 8N_{21} + 4N_{22} + 4N_{23} + 4N_{24} \end{aligned}$$

is transformed into identity, i.e.,  $0 = 0$ . The balance (9) can be rewritten into equivalent forms:

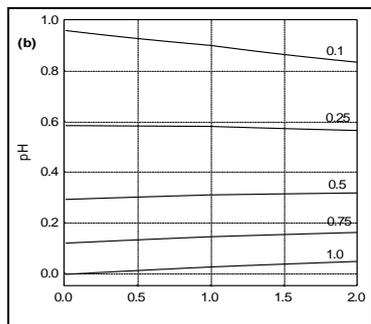
$$\begin{aligned} 2 \cdot f_2 - f_1 + f_0 - 6 \cdot f_3 - 4 \cdot f_4 - 4 \cdot f_5 = 0 \quad | \cdot (-1) &\Leftrightarrow (+1) \cdot f_1 + (-2) \cdot f_2 + (+6) \cdot f_3 + (+4) \cdot f_4 + (+4) \cdot f_5 - f_0 = 0 \\ (+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+6) \cdot f(\text{SO}_4) + (+4) \cdot f(\text{CO}_3) + (+4) \cdot f(\text{Ce}) - \text{ChB} &= 0 \quad (10) \end{aligned}$$

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

#### The D subsystem

We get here the balances:

$$\begin{aligned} f_0 &= \text{ChB} \\ N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 2N_9 + N_{10} &= 0 \quad (11) \\ f_1 &= f(\text{H}) \\ 2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_9n_9 + N_{10}(1+2n_{10}) + 2N_{11}n_{11} &= 14N_{05} + 2N_{06} + 2N_{07} \\ f_2 &= f(\text{O}) \\ N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_9n_9 + N_{10}(1+n_{10}) + N_{11}(4+n_{11}) &= 11N_{05} + 4N_{06} + N_{07} + 2N_{08} \\ -f_3 &= -f(\text{SO}_4) \\ N_{05} + N_{06} &= N_4 + N_5 + N_{11} \\ -f_4 &= -f(\text{CO}_3) \\ N_{08} &= N_6 + N_7 + N_8 \quad (12) \\ -f_5 &= -f(\text{Fe}) \\ N_{05} &= N_9 + N_{10} + N_{11} \\ f_{12} &= 2 \cdot f_2 - f_1 \\ -N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} &= 8N_{05} + 6N_{06} + 4N_{08} \end{aligned}$$



**Figure 3:** The pH = pH(Φ) relationship for the D+T system at  $V_0 = 100$ ,  $C_0 = 0.01$ ,  $C = 0.1$ ,  $C_1 = 0.5$  and different  $C_{01}$  values indicated at the corresponding lines.

The linear combination

$$f_{12} - 6 \cdot f_3 - 4 \cdot f_4 - 2 \cdot f_5 = 0 \tag{13}$$

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 (11) can be rewritten into equivalent forms

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

$$(+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+6) \cdot f(\text{SO}_4) + (+4) \cdot f(\text{CO}_3) + (+2) \cdot f(\text{Fe}) - \text{ChB} = 0 \tag{14}$$

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

### The D+T system

For the D+T system we have the balances:

$$f_0 = \text{ChB}$$

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

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

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

$$N_{10}(1+2n_{10}) + 2N_{11}n_{11} + 2N_{12}n_{12} + N_{13}(1+2n_{13}) + N_{14}(2+2n_{14}) + N_{15}(2+2n_{15}) + 2N_{16}n_{16} + 2N_{17}n_{17} + 2N_{18}n_{18} + N_{19}(1+2n_{19}) + N_{20}(3+2n_{20}) + N_{21}(4+2n_{21}) + 2N_{22}n_{22} + 2N_{23}n_{23} + 2N_{24}n_{24} + 2N_{25}n_{25} + N_{26}(1+2n_{26}) + 2N_{27}n_{27} + 2N_{28}n_{28} + 2N_{29}n_{29} = 8N_{01} + 2N_{02} + 2N_{03} + 14N_{05} + 2N_{06} + 2N_{07}$$

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

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

$$-f_3 = -f(\text{SO}_4)$$

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

$$-f_4 = -f(\text{CO}_3)$$

$$N_{04} + N_{08} = N_6 + N_7 + N_8 \tag{17}$$

$$-f_5 = -f(\text{Fe})$$

$$N_{05} = N_9 + N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17} \tag{18}$$

$$-f_6 = -f(\text{Ce})$$

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

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

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

The linear combination

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

$$(+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+6) \cdot f(\text{SO}_4) + (+4) \cdot f(\text{CO}_3) - \text{ChB} = 0 \tag{21}$$

Involving  $K^*=4$  elemental balances for electron-non-active elements: H, O, S, C ( $f(\text{SO}_4) = f(\text{S})$ ,  $f(\text{CO}_3) = f(\text{C})$ ) is the simple sum of collected balances:

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

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

$$12N_{01} + 6N_{02} + 6N_{05} + 6N_{06} = 6N_4 + 6N_5 + 6N_{11} + 6N_{16} + 12N_{17} + 6N_{22} + 12N_{23} + 18N_{24} + 6N_{27} + 12N_{28} + 18N_{29} \quad 4N_{04} + 4N_{08} = 4N_6 + 4N_7 + 4N_8$$

It gives the equation

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

Denoting atomic numbers:  $Z_{\text{Fe}} = 26$ ,  $Z_{\text{Ce}} = 58$ , from Equations: 18,

19 and 22, we obtain the balance

$$\begin{aligned} & Z_{Fe} \cdot f_5 + Z_{Ce} \cdot f_6 - (2 \cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4) \\ & (Z_{Fe} - 2) \cdot (N_9 + N_{10} + N_{11}) + (Z_{Fe} - 3) \cdot (N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17}) + \\ & (Z_{Ce} - 4) \cdot (N_{18} + N_{19} + 2N_{20} + 2N_{21} + N_{22} + N_{23} + N_{24}) + \\ & (Z_{Ce} - 3) \cdot (N_{25} + N_{26} + N_{27} + N_{28} + N_{29}) \\ & = (Z_{Fe} - 2) \cdot N_{05} + (Z_{Ce} - 4) \cdot N_{01} \end{aligned} \quad (23)$$

Applying the relations:

$$\begin{aligned} [X_i^{Z_i}] \cdot (V_0 + V) &= 10^3 \cdot \frac{N_i}{N_A}, C_0 V_0 = 10^3 \cdot N_{01} / N_A, \text{ and} \\ CV &= 10^3 \cdot N_{05} / N_A \end{aligned} \quad (24)$$

in Eq. 23, we obtain the equation for GEB, written in terms of molar concentrations

$$\begin{aligned} & (Z_{Fe} - 2) \cdot ([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) + (Z_{Fe} - 3) \cdot ([Fe^{+3}] + [FeOH^{+2}] + \\ & [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] \\ & + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}]) + (Z_{Ce} - 4) \cdot ([Ce^{+4}] + [CeOH^{+3}] + \\ & 2 [Ce_2(OH)_3^{+5}] + 2 [Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] \\ & + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) + (Z_{Ce} - 3) \cdot ([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] \\ & + [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}]) = ((Z_{Fe} - 2) \cdot C_0 V_0 + (Z_{Ce} - 4) \cdot CV) / (V_0 + V) \end{aligned} \quad (23a)$$

Other linear combinations are also possible. Among others, we obtain the simpler form of GEB  $3f_5 + 3f_6 - (f_{12} + f_0 - 6f_3 - 4f_4) = 0$

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

$$\begin{aligned} & [Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] - ([Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2 \\ & [Ce_2(OH)_4^{+4}] + \\ & [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}]) = (C_0 V_0 - CV) / (V_0 + V) \end{aligned} \quad (25a)$$

From Eq. 20, considered as the primary form of Generalized Electron Balance (GEB),  $f_{12} = pr\text{-GEB}$ , we obtain the equation

$$\begin{aligned} & - [H^{+1}] + [OH^{-1}] + 7[HSO_4^{-1}] + 8[SO_4^{-2}] + 4[H_2CO_3] + 5[HCO_3^{-1}] \\ & + 6[CO_3^{-2}] + [FeOH^{+1}] + 8[FeSO_4] + [FeOH^{+2}] + 2[Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] \\ & + 8[FeSO_4^{+1}] + 16[Fe(SO_4)_2^{-1}] + [CeOH^{+3}] + 3[Ce_2(OH)_3^{+5}] + 4[Ce_2(OH)_4^{+4}] \\ & + 8[CeSO_4^{+2}] + 16[Ce(SO_4)_2] + 24[Ce(SO_4)_3^{-2}] + \\ & [CeOH^{+2}] + 8[CeSO_4^{+1}] + 16[Ce(SO_4)_2^{-1}] + 24[Ce(SO_4)_3^{-3}] \\ & = (16CV + 6(C_{01}V_0 + C_1V) + 4(C_{02}V_0 + C_2V)) / (V_0 + V) \end{aligned} \quad (20a)$$

where, in addition to Equations 24, we apply

$$C_1 V = 10^3 \cdot \frac{N_{02}}{N_A}, C_{01} V_0 = 10^3 \cdot \frac{N_{06}}{N_A}, C_2 V = 10^3 \cdot \frac{N_{04}}{N_A}, C_{02} V_0 = 10^3 \cdot \frac{N_{08}}{N_A} \quad (26)$$

From Eq. 22 we have

$$\begin{aligned} & 2 \cdot ([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) + 3 \cdot ([Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] \\ & + 2[Fe_2(OH)_2^{+4}] \\ & + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}]) + 4 \cdot ([Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + \end{aligned}$$

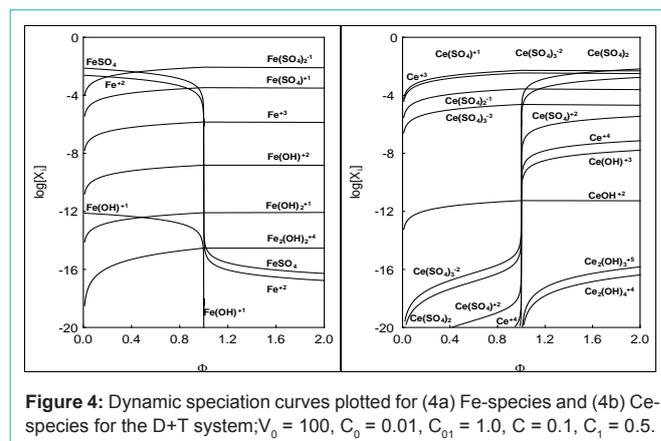


Figure 4: Dynamic speciation curves plotted for (4a) Fe-species and (4b) Ce-species for the D+T system;  $V_0 = 100$ ,  $C_0 = 0.01$ ,  $C_{01} = 1.0$ ,  $C = 0.1$ ,  $C_1 = 0.5$ .

$$\begin{aligned} & 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] \\ & + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}] + 3 \cdot ([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + \\ & [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}]) \\ & = (2 \cdot C_0 V_0 + 4 \cdot CV) / (V_0 + V) \end{aligned} \quad (22a)$$

As we see, the linear combination

$$f_{12} + f_0 - 6f_3 - 4f_4 = 0$$

Composed of  $f_{12}$  with  $f_0$  and the balances for electron-non-active elements, gives the Equations 22a and 23a, containing only the components and species where electron-active elements (here: Fe, Ce) are involved. The coefficients/multipliers at the concentrations in Eq. 22a are equal to oxidation numbers of the corresponding components and species with the electron-active elements involved.

The linear combination of Equations: 18 (multiplied by 2), 19 (multiplied by 4) and 22 gives the next/shortest form of GEB

$$\begin{aligned} & [Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + \\ & [Fe(SO_4)_2^{-1}] - ([Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + \\ & [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}]) = 0 \end{aligned} \quad (27)$$

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

Equations 20a, 22a, 23a, 25a and 27, are equivalent to each other. All them have full properties of the GEB, obtained according to Approach II to GEB, discussed widely in [4] and in some references cited therein. Other linear combinations of the balance  $f_{12}$  with  $f_0$ ,  $f_3, \dots, f_6$  are also acceptable/possible, from algebraic viewpoint. In particular, Eq. 19a is identical with the one obtained according to Approach I to GEB, based on the "card game" principle, described convincingly and illustrated artfully in [4] (pp. 41-43).

Briefly, according to Approach I to GEB, the common pool of electrons, introduced by Fe and Ce as the electron-active elements as 'players' [4], 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. 23. This way, the equivalency of Approaches I and II to GEB is proved.

For calculation purposes, the GEB, e.g. Eq. 27, is completed by charge and concentrations balances, obtained from Equations 15-17 and relations 22, 24:

$$[H^{+1}] - [OH^{-1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] - [HCO_3^{-1}] - 2[CO_3^{-2}] + 2[Fe^{+2}] + [FeOH^{+1}] +$$

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

$$4[Ce^{+4}] + 3[CeOH^{+3}] + 5[Ce_2(OH)_3^{+5}] + 4[Ce_2(OH)_4^{+4}] + 2[CeSO_4^{+2}] - 2[Ce(SO_4)_3^{-2}] +$$

$$3[Ce^{+3}] + 2[CeOH^{+2}] + [CeSO_4^{+1}] - [Ce(SO_4)_2^{-1}] - 3[Ce(SO_4)_3^{-3}] = 0 \quad (15a)$$

$$[HSO_4^{-1}] + [SO_4^{-2}] + [FeSO_4] + [FeSO_4^{+1}] + 2[Fe(SO_4)_2^{-1}] + [CeSO_4^{+2}] + 2[Ce(SO_4)_3^{-2}] +$$

$$3[Ce(SO_4)_3^{-2}] + [CeSO_4^{+1}] + 2[Ce(SO_4)_2^{-1}] + 3[Ce(SO_4)_3^{-3}] - (C_0V_0 + C_{01}V_0 + 2CV + C_1V)/(V_0+V) = 0 \quad (16a)$$

$$[H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] - (C_{02}V_0 + C_2V)/(V_0+V) = 0 \quad (17a)$$

$$[Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] + [Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}] - C_0V_0/(V_0+V) = 0 \quad (18a)$$

$$[Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}] + [Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}] - CV/(C_0+V) = 0 \quad (19a)$$

Independent equilibrium constants for this system are involved in relations:

$$[H^{+1}][OH^{-1}] = 10^{-14.0}; [HSO_4^{-1}] = 10^{1.8}[H^{+1}][SO_4^{-2}]; [H_2CO_3] = 10^{16.4}[H^{+1}]^2[CO_3^{-2}]; [HCO_3^{-1}] = 10^{10.1}[H^{+1}][CO_3^{-2}]; [Fe^{+3}] = [Fe^{+2}] \cdot 10^{A(E-0.771)}; [Ce^{+4}] = [Ce^{+3}] \cdot 10^{A(E-1.70)}; [FeOH^{+1}] = 10^{4.5}[Fe^{+2}]$$

$$[OH^{-1}]; [FeOH^{+2}] = 10^{11.0}[Fe^{+3}][OH^{-1}]; [Fe(OH)_2^{+1}] = 10^{21.7}[Fe^{+3}]$$

$$[OH^{-1}]^2; [Fe_2(OH)_2^{+4}] = 10^{21.7}[Fe^{+3}]^2[OH^{-1}]^2; [FeSO_4] = 10^{2.33}[Fe^{+2}][SO_4^{-2}]; [FeSO_4^{+1}] = 10^{4.18}[Fe^{+3}][SO_4^{-2}];$$

$$[Fe(SO_4)_2^{-1}] = 10^{7.4}[Fe^{+3}][SO_4^{-2}]^2; [CeOH^{+2}] = 10^{5.0}[Ce^{+3}][OH^{-1}]; [CeOH^{+3}] = 10^{13.3}[Ce^{+4}][OH^{-1}];$$

$$[Ce_2(OH)_3^{+5}] = 10^{13.3}[Ce^{+4}]^2[OH^{-1}]^3; [Ce_2(OH)_4^{+4}] = 10^{40.3}[Ce^{+4}]^2[OH^{-1}]^3; [Ce_2(OH)_4^{+4}] = 10^{53.7}[Ce^{+4}]^2[OH^{-1}]^4;$$

$$[CeSO_4^{+1}] = 10^{1.63}[Ce^{+3}][SO_4^{-2}]; [Ce(SO_4)_2^{-1}] = 10^{2.34}[Ce^{+3}][SO_4^{-2}]^2; [Ce(SO_4)_3^{-3}] = 10^{3.08}[Ce^{+3}][SO_4^{-2}]^3;$$

$$[CeSO_4^{+2}] = 10^{3.5}[Ce^{+4}][SO_4^{-2}]; [Ce(SO_4)_2] = 10^{8.0}[Ce^{+4}][SO_4^{-2}]^2;$$

$$[Ce(SO_4)_3^{-2}] = 10^{10.4}[Ce^{+4}][SO_4^{-2}]^3 \quad (28)$$

In this case, the number  $K=6$  of the basic variables  $x_k$  is equal to the number of balances, see 15a – 19a and e.g. 25a, where

$$x = [x_1, \dots, x_6]^T = [E, pH, pCe3, pFe2, pSO4, pH2CO3]^T \quad (29)$$

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 variables appear in the exponents of the power of 10, namely

$$\begin{aligned} [e^{-1}] &= 10^{-AE}, [H^{+1}] = 10^{-pH}, [Ce^{+3}] = 10^{-pCe3}, \\ [Fe^{+2}] &= 10^{-pFe2}, [SO_4^{-2}] = 10^{-pSO4}, [H_2CO_3] = 10^{-pH2CO3} \end{aligned} \quad (30)$$

where  $A = F/(RT \cdot \ln 10) = 16.9$  for  $T = 298$  K.

## Graphical Presentation of Results and Discussion

The results of calculations realized for D+T system with use of MATLAB are presented in Figures 2-4 [19]. Figure 2a shows the redox titration curves  $E = E(\Phi)$  in the D+T system, at different concentrations  $C_{01}$  of  $H_2SO_4$  contained in the titrand (D). Some fragments of the curves, related to  $\Phi < \Phi_{eq}$  and  $\Phi > \Phi_{eq}$  are presented in extended scale in Figures 2b,c. The jump on the curve occurs at  $\Phi = \Phi_{eq} = 1$ , i.e., at the equivalent point where  $C \cdot V_{eq} = C_0 \cdot V_0$ . Points  $(V_j, E_j)$  in the jump region were obtained by performing subsequent iterations at a reduced steps,  $V_{j+1} - V_j$ , corresponding to subsequent titrant additions.

Figure 3 shows the  $pH = pH(\Phi)$  functions  $CV_{eq} = C_0V_0$  obtained under the same conditions ( $C_0, C_{01}, C, C_1$ ), at which the curves in Figure 2 were plotted. The curves  $pH = pH(\Phi)$  do not show any visible bend in the vicinity of  $\Phi = \Phi_{eq} = 1$ . It can be explained as the consequence of high buffer capacity of the solution [20], resulting from the presence of strong acid ( $H_2SO_4$ ), with total concentration  $(C_{01}V_0 + C_1V)/(V_0+V)$ , compare with the related plots in [14,21-23]. The direction of changes in the course of the respective curves in figure 3 results from the difference between concentrations  $C_{01}$  (in D) and  $C_1$  in T; at  $C_1 < C_{01}$ , the diluting effect from the titrant side is marked, which results in a small (relative) decrease of pH value.

Figures 4a,b show speciation graphs for Fe and Ce species in the system. All the species involved in concentration balances for Fe (Eq. 18a) and Ce (Eq. 19a), are presented there. In particular,  $[Fe^{+3}] \ll [Fe(SO_4)_2^{-1}]$ ,  $[Ce^{+4}] \ll [Ce(SO_4)_3^{-2}]$ ,  $[Fe^{+2}] < [FeSO_4]$  and  $[Ce^{+3}] \approx [CeSO_4^{+1}]$ , i.e., simple ions:  $Ce^{+4}$ ,  $Fe^{+3}$ ,  $Fe^{+2}$  and  $Ce^{+3}$  are not predominant species in the system, also in the vicinity of  $\Phi_{eq} = 1$ .

## Final Comments

Redox systems are the most important and most complex electrolytic systems. 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 approach, where the systems of different complexity are elaborated in a uniform manner according to GATES principles [4], formulated by Michałowski (1992).

When related to redox systems, the acronym GATES/GEB ∈ GATES is applied. The GATES/GEB is perceived as the best possible thermodynamic approach to redox systems, and the GEB is the law of Nature. The GEB, discovered by Michałowski, and formulated as the Approaches I (1992) and II (2005) to GEB, is fully compatible with charge and concentration balances, and relations for the corresponding equilibrium constants. 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 Generalized Electron Balance (GEB) are equivalent, i.e.,

Approach I to GEB ⇔ Approach II to GEB

In other words, both Approaches are mutually transformable, according to linear combination procedure.

The Approach I is based on the principle of common pool of electrons involved with electron-active elements [4], whereas the Approach II originates from the linear combination  $f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(\text{O}) - f(\text{H})$  of elemental balances:  $f_1 = f(\text{H})$  for H, and  $f_2 = f(\text{O})$  for O, formulated for a redox system. For a non-redox systems,  $2 \cdot f(\text{O}) - f(\text{H})$  is a linear combination of other balances: charge balance  $f_0 = \text{ChB}$ , and elemental/core balances  $f_k = f(Y_k)$  ( $k=3, \dots, K$ ), where element/core  $Y_k \neq \text{H}, \text{O}$ . For a redox system,  $f_0, f_{12}, f_3, \dots, f_k$  is a set of K linearly independent equations, whereas for a non-redox system we have the set of  $K - 1$  linearly independent equations  $f_0, f_3, \dots, f_k$ .

When compared with the Approach I, the Approach II to GEB offers several advantages, however. Although derivation of GEB according to the Approach II is more laborious (time-consuming), it enables to formulate this balance without prior knowledge of ON's for the elements, involved frequently in complex components and species of the system. Only the composition (expressed by chemical formula) of components forming the system and composition of the species formed in the system, together with their external charges, are required, i.e., 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 [27]. Anyway, the oxidation number/state, perceived from the viewpoint of IUPAC definition [39], and representing the of an element in a compound or 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 when applied to complex organic species in redox systems of biological origin [40-44]. The Approach II to GEB is advantageous /desired, inter alia, for redox systems where radical and ion-radical species are formed. What is more, the players and fans, as ones perceived from the Approach I to GEB viewpoint [1], are not indicated a priori within the Approach II to GEB. 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 Approaches I and 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  $f_{12} = 2 \cdot f(\text{O}) - f(\text{H})$  is the primary form of GEB indicates clearly the exquisite role of H and O in redox systems, especially in aspect insignificantly small concentrations of free electrons, as those calculated and discussed in [12] (pp. 361-363).

To check the linear dependency of equations related to a non-redox system, the transformation of the linear combination into identity,  $0 = 0$ , is suggested. For this purpose, we formulate the linear combination (Eq. 6)

$$\sum_{k=1}^K d_k \cdot f_k - f_0 = 0 \quad (31)$$

where  $d_1 = +1$ ,  $d_2 = -2$ . In general,  $d_k$  is equal to (or involved with) the oxidation numbers of the k-th element in the corresponding component and species. The multipliers  $d_k$  ( $k=1, 2, 3, \dots, K$ ) enable to get the desired form of the linear combination: for a non-redox system, the desired linear combination is the identity  $0 = 0$ , whereas for a redox system it is the simpler form of the linear combination, e.g., Eq. 25a or Eq. 27.

When the D and T are mixed, the redox reactions occur in the D+T mixture. In this paper, the D+T mixture is formed gradually, according to titrimetric mode, where T is added dropwise into D.

In the redox D+T system considered here, we have Fe and Ce as players, and H, O, S, C as fans. Generally, in the set of K elements of the system we have  $K^*$  fans, and  $K - K^*$  players. Applying the summation

$$\sum_{k=1}^{K^*} d_k \cdot f_k - f_0 = 0 \quad (32)$$

we get the simpler form of the linear combination, where the multipliers for the numbers/concentrations of the species and components containing the players are equal to ON's for elements in these species and components, see Equations 22 and 22a; the components and species composed only from fans are not involved in Equations 22 and then in 22a. This regularity is valid for any redox system. For a non-redox system ( $K^* = K$ ), Eq. 30 is transformed into identity,  $0 = 0$ . For any redox system, Eq. 32 is different from the identity. The identity  $0 = 0$  is the useful criterion of linear dependence of balances. The set of K balances  $f_0, f_{12}, f_3, \dots, f_k$  is mutually independent for redox systems, or mutually dependent for non-redox systems. This is the general criterion distinguishing between redox and non-redox system. For a non-redox system,  $K - 1$  independent balances  $f_0, f_3, \dots, f_k$  are formulated. These regularities are obligatory for static and dynamic systems. In all instances, the balances are ultimately expressed in terms of molar concentrations of compounds and species. This results from the fact that the equilibrium constants are expressed in terms of molar concentrations of the species.

The GATES provides the powerful tool necessary for thermodynamic description of equilibrium, non-equilibrium, and metastable, redox and non-redox, mono- and two-phase systems of any degree of complexity, with the possibility of all attainable/pre-selected physicochemical knowledge to be involved, with none

simplifying assumptions done for calculation purposes, where different types of reactions occur in batch or dynamic systems. In all instances, one can check/follow measurable quantities (potential E, pH) in dynamic and static processes and gain the information about details not measurable in real experiments; it particularly refers to dynamic speciation. Different “variations on the subject” are also possible; it particularly refers to metastable redox systems [1,8]. GATES/GEB is also the first step for resolution of kinetic systems, e.g. ones where oscillation reactions occur [1].

Formulation of GATES and GATES/GEB [20,40,41] has allowed to sort out many important concepts, based previously on the stoichiometry of a reaction. And so, the Generalized Equivalent Mass (GEM) concept, also introduced by Michałowski (1979), has been suggested [9], with none relevance to a chemical reaction notation. The formulation of dynamic buffer capacities for redox systems [30] is fully compatible with the dynamic buffer capacity related to the systems, where only acid-base equilibria are involved [38,45,46].

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