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A Distinguishing Feature of the Balance 2•f(O)–f(H) in Electrolytic Systems: The Reference to Titrimetric Methods of Analysis

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Additional information is available at the end of the chapter

Motto: 'Nothing is too wonderful to be true if it be consistent with the laws of Nature'
(M. Faraday)

Abstract

The balance $2 \cdot f(O) - f(H)$ provides a general criterion distinguishing between electrolytic redox and non-redox systems of any degree of complexity, in aqueous, non-aqueous and mixed-solvent media. When referred to redox systems, it is an equation linearly independent on charge (ChB) and elemental/core balances $f(Y_g)$ for elements/cores $Y_g \neq H$ and O, whereas for non-redox systems, $2 \cdot f(O) - f(H)$ is linearly dependent on these balances. The balance $2 \cdot f(O) - f(H)$ formulated for redox systems is the primary form (pr-GEB) of the generalized electron balance (GEB) as the fundamental equation needed for resolution of these systems. Formulation of GEB for redox systems needs no prior knowledge of oxidation numbers for all elements of the system. Any prior knowledge of oxidation numbers for all elements in components forming a redox system and in the species of the system thus formed is not necessary within the Approach II to GEB. Oxidants and reductants are not indicated. Stoichiometry and equivalent mass are redundant concepts only. The GEB, together with charge balance and concentration balances for elements $\neq$ H and O, and the complete set of independent equations for equilibrium constants form an algorithm, resolvable with use of an iterative computer program. All attainable physicochemical knowledge can be included in the algorithm. Some variations involved with tests of possible reaction paths for metastable systems can also be made. The effects of incomplete physicochemical knowledge on the system can be also tested. One of the main purposes of this chapter is to provide the GEB formulation needed for resolution of redox systems and familiarize it to a wider community of chemists.

Keywords: electrolytes, redox systems, non-redox systems, generalized electron balance (GEB), titration

1. Introduction

Scientific theories describe particular units and rules governing the relationships between them. This description is considered as interpretation of reality. In particular, the thermodynamic description of any electrolytic system according to generalized approach to electrolytic systems (GATESs) [1] is based on fundamental and physical rules of conservation, expressed by charge balance (ChB) and elemental balances, for particular elements and/or cores in a closed system, separated from the environment by diathermal (freely permeable by heat) walls. The term 'core' is related to a cluster of elements with the same formula, structure and external charge. For example, $HSO_4^{-1} \cdot n_5 H_2O$, $SO_4^{-2} \cdot n_6 H_2O$ and $FeSO_4 \cdot n_{27} H_2O$, in Eq. (3) (below), have the common core (SO_4^{-2}). In this context, the pairs of species: (i) $C_2O_4^{-2}$ and CO_3^{-2}; (ii) $C_2O_4^{-2}$ (from maleic acid) and $C_2O_4^{-2}$ (from fumaric acid) and (iii) NO_2^{-1} and NO_2 have no common cores.

Chemical interactions in electrolytic systems, for example protonation, neutralization, hydration, hydrolysis or dilution phenomena, are usually accompanied by exothermic or endothermic effects. However, the mass change, Δm, resulting from these thermal phenomena, estimated according to the Einstein's formula $\Delta E = \Delta m \cdot c^2$ and put in context with their enthalpies ΔH ($\Delta E = \Delta H$), that is $\Delta m = \Delta H/c^2$, is negligibly small (not measurable). Therefore, the mass of a chemical system remains practically unchanged, regardless of whether the chemical reactions take place in it or not.

The heat exchange between the system and its environment through diathermal walls enables the temperature T of the system to be kept constant during the appropriate dynamic processes, such as titration, performed in a quasistatic manner. Stability of temperature T within the titrant (titrating solution, T), titrand (titrated solution, D) and D + T mixture, together with constancy of ionic strength (I) in D+T, is the preliminary condition ensuring stability of the corresponding equilibrium constants, $K_i = K_i(T, I)$, related to the system in question. The diathermal walls separate condensed (liquid or liquid + solid) phases from their environment.

An open chemical system is an approximation of the closed system—provided that the matter (e.g., H_2O, CO_2 and O_2) exchange between the system and its surroundings can be neglected, within a relatively short period of time needed to carry out the process considered, for example, titration.

On the initial stage of ChB and elemental/core balance formulation, it is advisable to start the quantitative considerations from the numbers of particular entities (components, species):

- N_{0j} for jth component constituting the system

- N_i for ith species in the system thus formed

For example, H_2O and gaseous HCl, as components, form an aqueous solution of HCl, with H_2O and hydrates of H^{+1}, OH^{-1} and Cl^{-1} as the species. Generally, when solid, liquid and/or gaseous solutes are introduced into water, a mono- or two-phase system is obtained. The resulting mixture is limited to the condensed (liquid or liquid + solid) phases. We refer mainly to aqueous media (W = H_2O), where the physicochemical knowledge is relatively extensive, incomparably better than that for the system with non-aqueous, or mixed-solvent media [2–6],

with amphiprotic co-solvents involved, which is also considered in this chapter. For such media, the elemental $f(E_g)$) or core $f(core_g)$) balances written in terms of numbers of individual entities containing the elements (E_g) or cores ($core_g$), are formulated.

In aqueous electrolytic systems, different entities $X_i^{z_i}$ exist as hydrated species, $X_i^{z_i} \cdot n_i H_2O$; $n_i = n_{iW} = n_i H_2O$ is the mean number of water (W = H_2O) molecules attached to $X_i^{z_i}(n_i \geq 0)$, z_i is a charge of this species, expressed in elementary charge units and e = F/N_A (F = Faraday constant, N_A = Avogadro number). For these species present in static or dynamic systems, we apply the notation

$$X_i^{z_i}(N_i, n_i) \tag{1}$$

where N_i is the number of these entities (individual species). On this basis, the numbers of particular elements in these species are calculated; for example, in the solution II (see below), N_{04} molecules of $FeSO_4 \cdot 7H_2O$ contain 14 N_{04} atoms of H, 11 N_{04} atoms of O and N_{11} atoms of Fe; N_5 ions of $HSO_4^{-1} \cdot n_5 H_2O$ (N_5, n_5) in the set (2) of species specified below contain $N_5(1 + 2n_5)$ atoms of H, $N_5(4 + n_5)$ atoms of O and N_5 atoms of S.

In further parts of this chapter, the terms linear combination and linear dependency/independency of equations are introduced. These terms, well known from the elementary algebra course, will be applied to elemental/core balances, as a system of algebraic equations. The elemental balances $f(H)$ for hydrogen (H) and $f(O)$ for oxygen (O) and the linear combination $2 \cdot f(O) - f(H)$ are formulated and then combined with charge balance (ChB) and other elemental/core balances $f(Y_g)$ for other elements ($Y_g = E_g$) or cores ($Y_g = core_g$), $Y_g \neq$ H and O. This way, the general properties of $2 \cdot f(O) - f(H)$ in non-redox and redox systems are distinguished, see Refs. [7–18] and earlier references cited therein.

The $2f(O) - f(H)$, charge balance and elemental/core balances will be expressed first in terms of the numbers of particular entities. Next, the related balances will be presented in terms of molar concentrations, to be fully compatible with expressions for equilibrium constants that are also presented in terms of molar concentrations of the related species.
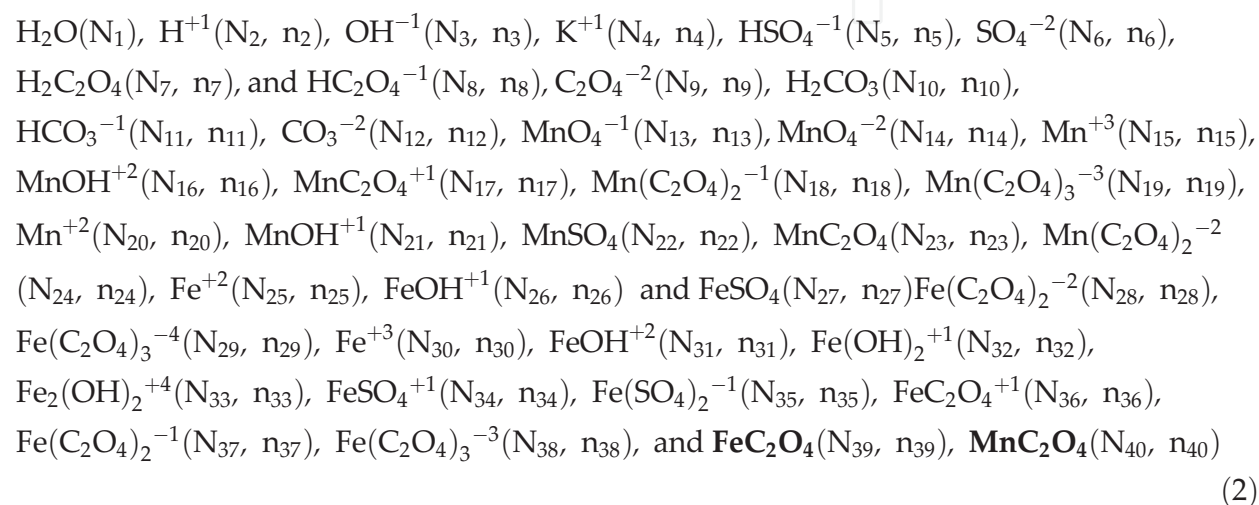
Static and dynamic systems are distinguished. A static system is obtained after disposable mixing with the respective components. For illustrative purposes, we consider first four solutions, as static non-redox systems, formed from the following components:

- (I) N_{01} molecules of $KMnO_4$, N_{02} molecules of CO_2 and N_{03} molecules of H_2O in V_1 mL of the resulting solution

- (II) N_{04} molecules of $FeSO_4 \cdot 7H_2O$, N_{05} molecules of H_2SO_4, N_{06} molecules of CO_2 and N_{07} molecules of H_2O in V_2 mL of the resulting solution

- (III) N_{08} molecules of $H_2C_2O_4 \cdot 2H_2O$, N_{09} molecules of H_2SO_4, N_{010} molecules of CO_2 and N_{011} molecules of H_2O in V_3 mL of the resulting solution

- (IV) N_{012} molecules of $FeSO_4 \cdot 7H_2O$, N_{013} molecules of $H_2C_2O_4 \cdot 2H_2O$, N_{014} molecules of H_2SO_4, N_{015} molecules of CO_2 and N_{016} molecules of H_2O in V_4 mL of the resulting solution.

The CO_2 in the respective solutions is primarily considered as one originated from ambient air, on the step of preparation of these solutions.

From these static systems, we prepare later different dynamic systems: (I) $\Rightarrow$ (II), (I) $\Rightarrow$ (III) and (I) $\Rightarrow$ (IV), where (I) as titrant T is added into (II), (III) or (IV) as titrand D (T $\Rightarrow$ D), and the D + T mixtures containing different species are formed.

To avoid a redundancy resulting from application of different subscripts within (N_i, n_i) ascribed to the same species $X_i^{z_i} \cdot n_i H_2O$ in different solutions (I)–(IV), we apply the common basis of the species from which the components will be selected to the respective balances. The set of the species is as follows:

$H_2O(N_1)$, $H^{+1}(N_2, n_2)$, $OH^{-1}(N_3, n_3)$, $K^{+1}(N_4, n_4)$, $HSO_4^{-1}(N_5, n_5)$, $SO_4^{-2}(N_6, n_6)$, $H_2C_2O_4(N_7, n_7)$, and $HC_2O_4^{-1}(N_8, n_8)$, $C_2O_4^{-2}(N_9, n_9)$, $H_2CO_3(N_{10}, n_{10})$, $HCO_3^{-1}(N_{11}, n_{11})$, $CO_3^{-2}(N_{12}, n_{12})$, $MnO_4^{-1}(N_{13}, n_{13})$, $MnO_4^{-2}(N_{14}, n_{14})$, $Mn^{+3}(N_{15}, n_{15})$, $MnOH^{+2}(N_{16}, n_{16})$, $MnC_2O_4^{+1}(N_{17}, n_{17})$, $Mn(C_2O_4)_2^{-1}(N_{18}, n_{18})$, $Mn(C_2O_4)_3^{-3}(N_{19}, n_{19})$, $Mn^{+2}(N_{20}, n_{20})$, $MnOH^{+1}(N_{21}, n_{21})$, $MnSO_4(N_{22}, n_{22})$, $MnC_2O_4(N_{23}, n_{23})$, $Mn(C_2O_4)_2^{-2}$ (N_{24}, n_{24}), $Fe^{+2}(N_{25}, n_{25})$, $FeOH^{+1}(N_{26}, n_{26})$ and $FeSO_4(N_{27}, n_{27})Fe(C_2O_4)_2^{-2}(N_{28}, n_{28})$, $Fe(C_2O_4)_3^{-4}(N_{29}, n_{29})$, $Fe^{+3}(N_{30}, n_{30})$, $FeOH^{+2}(N_{31}, n_{31})$, $Fe(OH)_2^{+1}(N_{32}, n_{32})$, $Fe_2(OH)_2^{+4}(N_{33}, n_{33})$, $FeSO_4^{+1}(N_{34}, n_{34})$, $Fe(SO_4)_2^{-1}(N_{35}, n_{35})$, $FeC_2O_4^{+1}(N_{36}, n_{36})$, $Fe(C_2O_4)_2^{-1}(N_{37}, n_{37})$, $Fe(C_2O_4)_3^{-3}(N_{38}, n_{38})$, and $\mathbf{FeC_2O_4}(N_{39}, n_{39})$, $\mathbf{MnC_2O_4}(N_{40}, n_{40})$

$$\text{(2)}$$

2. A short note

Referring to pure algebra, let us consider the set of G + 1 algebraic equations: $f_g(\mathbf{x}) = \varphi_g(\mathbf{x}) - b_g = 0$, where g = 0,1,…,G, $\mathbf{x}^T = (x_1,…,x_I)$, transposed (^{T}) vector $\mathbf{x}$, composed of independent (scalar) variables x_i (i $\in$ <1, I>); a_{gi}, $b_g \in \mathcal{R}$ are independent (explicitly) on $\mathbf{x}$. After multiplying the equations by the numbers $\omega_g \in \mathcal{R}$, and addition of the resulting equations, we get the linear combination $\sum_{g=0}^{G} \omega_g \cdot f_g(\mathbf{x}) = 0 \Leftrightarrow \sum_{g=0}^{G} \omega_g \cdot \varphi_g(\mathbf{x}) = \sum_{g=0}^{G} \omega_g \cdot b_g$ of the basic equations.

Formation of linear combinations is applicable to check the linear dependence or independence of the balances. A very useful/effective manner for checking/stating the linear dependence of the balances is the transformation of an appropriate system of equations to the identity 0 = 0 [2, 23]. For this purpose, we will try, in all instances, to obtain the simplest form of the linear combination. To facilitate these operations, carried out by cancellation of the terms on the left and right sides of equations after multiplying and changing sides of these equations, we apply the equivalent forms of the starting equations $f_g(\mathbf{x}) = 0$:

$$f_g(\mathbf{x}) : \varphi_g(\mathbf{x}) - b_g = 0 \Leftrightarrow \varphi_g(\mathbf{x}) = b_g \Leftrightarrow -f_g(\mathbf{x}) : -\varphi_g(\mathbf{x}) = -b_g \Leftrightarrow b_g = \varphi_g(\mathbf{x}). \tag{3}$$

In this notation, $f_g(\mathbf{x})$ will be essentially treated not as the algebraic expression on the left side of the equation $f_g(\mathbf{x}) = 0$ but as an equation that can be expressed in alternative forms presented above.

3. Combination of elemental/core balances for non-redox systems

For the solution (I), we have the balances:

$f_1 = f(H)$:

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

$f_2 = f(O)$:

$N_1 + N_2n_2 + N_3(1 + n_3) + N_4n_4 + N_{10}(3 + n_{10}) + N_{11}(3 + n_{11}) + N_{12}(3 + n_{12})$
$+ N_{13}(4 + n_{13}) = 4N_{01} + 2N_{02} + N_{03}$

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

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

$$f_0 = ChB : \qquad N_2 - N_3 + N_4 - N_{11} - 2N_{12} - N_{13} = 0$$
$$-f_3 = -f(K) : \qquad N_{01} = N_4$$
$$-7f_4 = -7f(Mn) : \qquad 7N_{01} = 7N_{13}$$
$$-4f_5 = -4f(CO_3) : \qquad 4N_{02} = 4N_{10} + 4N_{11} + 4N_{12}$$

$$f_{12} + f_0 - f_3 - 7f_4 - 4f_5 : \quad 0 = 0$$

For the solution (II), we have the balances:

$f_1 = f(H)$:

$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + N_5(1 + 2n_5) + 2N_6n_6 + N_{10}(2 + 2n_{10})$
$+ N_{11}(1 + 2n_{11}) + 2N_{12}n_{12} + 2N_{25}n_{25} + N_{26}(1 + 2n_{26}) + 2N_{27}n_{27} = 14N_{04} + 2N_{05} + 2N_{07}$

$f_2 = f(O)$:

$N_1 + N_2n_2 + N_3(1 + n_3) + N_5(4 + n_5) + N_6(4 + n_6) + N_{10}(3 + n_{10}) + N_{11}(3 + n_{11})$
$+ N_{12}(3 + n_{12}) + N_{25}n_{25} + N_{26}(1 + n_{26}) + N_{27}(4 + n_{27}) = 11N_{04} + 4N_{05} + 2N_{06} + N_{07}$

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

$-N_2 + N_3 + 7N_5 + 8N_6 + 4N_{10} + 5N_{11} + 6N_{12} + N_{26} + 8N_{27} = 8N_{04} + 6N_{05} + 4N_{06}$

$$f_0 = ChB : \qquad N_2 - N_3 - N_5 - 2N_6 - N_{11} - 2N_{12} + 2N_{25} + N_{26} = 0$$
$$-2f_3 = -2f(Fe) : \qquad 2N_{04} = 2N_{25} + 2N_{26} + 2N_{27}$$
$$-6f_4 = -6f(SO_4) : \qquad 6N_{04} + 6N_{05} = 6N_5 + 6N_6 + 6N_{27}$$
$$-4f_5 = -4f(CO_3) : \qquad 4N_{06} = 4N_{10} + 4N_{11} + 4N_{12}$$

$$f_{12} + f_0 - 2f_3 - 6f_4 - 4f_5 : \quad 0 = 0$$

For the solution (III), we have the balances:

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

$$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + N_5(1 + 2n_5) + 2N_6n_6 + N_7(2 + 2n_7) + N_8(1 + 2n_8)$$
$$+ 2N_9n_9 + N_{10}(2 + 2n_{10}) + N_{11}(1 + 2n_{11}) + 2N_{12}n_{12} = 6N_{08} + 2N_{09} + 2N_{011}$$

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

$$N_1 + N_2n_2 + N_3(1 + n_3) + N_5(4 + n_5) + N_6(4 + n_6) + N_7(4 + n_7) + N_8(4 + n_8)$$
$$+ N_9(4 + n_9) + N_{10}(3 + n_{10}) + N_{11}(3 + n_{11}) + N_{12}(3 + n_{12}) = 6N_{08} + 4N_{09} + 2N_{010} + N_{011}$$

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

$$-N_2 + N_3 + 7N_5 + 8N_6 + 6N_7 + 7N_8 + 8N_9 + 4N_{10} + 5N_{11} + 6N_{12} = 6N_{08} + 6N_{09} + 4N_{010}$$

$f_0 = \text{ChB}$: $\quad\quad\quad\quad\quad N_2 - N_3 - N_5 - 2N_6 - N_8 - 2N_9 - N_{11} - 2N_{12} = 0$

$-6f_3 = -6f(\text{SO}_4)$: $\quad\quad 6N_{09} = 6N_5 + 6N_6$

$-4f_4 = -4f(\text{CO}_3)$: $\quad\quad 4N_{010} = 4N_{10} + 4N_{11} + 4N_{12}$

$-6f_5 = -6f(\text{C}_2\text{O}_4)$: $\quad\quad 6N_{08} = 6N_7 + 6N_8 + 6N_9$

$f_{12} + f_0 - 6f_3 - 4f_4 - 6f_5$: $\quad 0 = 0$

For the solution (IV), we have the balances:

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

$$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + N_5(1 + 2n_5) + 2N_6n_6 + N_7(2 + 2n_7) + N_8(1 + 2n_8)$$
$$+ 2N_9n_9 + N_{10}(2 + 2n_{10}) + N_{11}(1 + 2n_{11}) + 2N_{12}n_{12} + 2N_{25}n_{25} + N_{26}(1 + 2n_{26}) + 2N_{27}n_{27}$$
$$+ 2N_{28}n_{28} + 2N_{29}n_{29} + 2N_{39}n_{39} = 14N_{012} + 6N_{013} + 2N_{014} + 2N_{016}$$

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

$$N_1 + N_2n_2 + N_3(1 + n_3) + N_5(4 + n_5) + N_6(4 + n_6) + N_7(4 + n_7) + N_8(4 + n_8) + N_9(4 + n_9)$$
$$+ N_{10}(3 + n_{10}) + N_{11}(3 + n_{11}) + N_{12}(3 + n_{12}) + N_{25}n_{25} + N_{26}(1 + n_{26}) + N_{27}(4 + n_{27})$$
$$+ N_{28}(8 + n_{28}) + N_{29}(12 + n_{29}) + N_{39}(4 + n_{39}) = 11N_{012} + 6N_{013} + 4N_{014} + 2N_{015} + N_{016}$$

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

$$-N_2 + N_3 + 7N_5 + 8N_6 + 6N_7 + 7N_8 + 8N_9 + 4N_{10} + 5N_{11} + 6N_{12} + N_{26} + 8N_{27} + 16N_{28}$$
$$+24N_{29} + 8N_{39} = 8N_{012} + 6N_{013} + 6N_{014} + 4N_{015}$$

$f_0 = \text{ChB}$:

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

$-6f_3 = -6f(\text{SO}_4)$: $\quad\quad 6N_{012} + 6N_{014} = 6N_5 + 6N_6 + 6N_{28}$

$-4f_4 = -4f(\text{CO}_3)$: $\quad\quad 4N_{015} = 4N_{10} + 4N_{11} + 4N_{12}$

$-6f_5 = -6f(\text{C}_2\text{O}_4)$: $\quad\quad 6N_{013} = 6N_7 + 6N_8 + 6N_9 + 12N_{28} + 18N_{29} + 6N_{39}$

$-2f_6 = -2f(\text{Fe})$: $\quad\quad 2N_{012} = 2N_{25} + 2N_{26} + 2N_{27} + 2N_{28} + 2N_{29} + 2N_{39}$

$f_{12} + f_0 - 6f_3 - 4f_4 - 6f_5 - 2f_6$: $\quad 0 = 0$

Summarizing, for all the solutions (I)–(IV), we obtain the identities 0 = 0:

$$(I)f_{12} + f_0 - f_3 - 7f_4 - 4f_5 = 0; \quad (II)f_{12} + f_0 - 2f_3 - 6f_4 - 4f_5 = 0; \quad (III)f_{12} + f_0 - 6f_3 - 4f_4 - 6f_5 = 0;$$
$$(IV)f_{12} + f_0 - 6f_3 - 4f_4 - 6f_5 - 2f_6 = 0$$

$$(4)$$

All the solutions are non-redox systems. Except protonation/hydrolytic effects in (I)–(IV), the complexation and precipitation occur in (II) and (IV); the precipitation of **FeC_2O_4** does not occur there at sufficiently high concentrations of H_2SO_4.

The solutions can be mixed according to titrimetric mode. In particular, we refer to the D + T systems obtained in the titrations T ⇒ D indicated above, namely (I) ⇒ (II), (I) ⇒ (III) and (I) ⇒ (IV). According to the notation applied elsewhere, for example, in Refs. [19–23], V_0 mL of D is titrated with volume V mL of T, added up to a given point of the titration, and the D + T mixture with volume $V_0 + V$ mL is formed at this point if the assumption of the volume additivity is valid.

We assume $V_1 = V$, $CV = 10^3 \cdot N_{01}/N_A$ (N_A: Avogadro's number) and $V_2 = V_0$ and $C_0V_0 = 10^3 \cdot N_{04}/N_A$ for (I) ⇒ (II); $V_3 = V_0$ and $C_0V_0 = 10^3 \cdot N_{08}/N_A$ for (I) ⇒ (III); $V_4 = V_0$ and $C_{01}V_0 = 10^3 \cdot N_{013}/N_A$ and $C_{02}V_0 = 10^3 \cdot N_{012}/N_A$ for (I) ⇒ (IV). Concentrations of the species $X_i^{z_i} \cdot n_iH_2O$ in the related systems are defined by relation $[X_i^{z_i}](V_0 + V) = N_i/N_A$, where $[X_i^{z_i}]$ is the molar concentration of $X_i^{z_i} \cdot n_iH_2O$ for $i \geq 2$. The progress of the titration in (I) ⇒ (II) and (I) ⇒ (III) can be defined by the fraction titrated [24–29] value

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

$$(5)$$

whereas V will be taken as a parameter varied on abscissa in the graphical presentation of the system (I) ⇒ (IV).

4. Formulation of dynamic redox systems

The D and T, formed out of particular components, are considered as subsystems of the D + T system thus obtained. The titration is considered as a quasistatic process carried out under isothermal conditions and perceived both from physicochemical and analytical viewpoints.

Let us consider four starting solutions composed of:

- N_{01} molecules of $KMnO_4$, N_{02} molecules of CO_2 and N_{03} molecules of H_2O in V_1 mL of the resulting solution

- N_{04} molecules of $FeSO_4 \cdot 7H_2O$, N_{05} molecules of H_2SO_4, N_{06} molecules of CO_2 and N_{07} molecules of H_2O in V_2 mL of the resulting solution

- N_{08} molecules of $H_2C_2O_4 \cdot 2H_2O$, N_{09} molecules of H_2SO_4, N_{010} molecules of CO_2 and N_{011} molecules of H_2O in V_3 mL of the resulting solution

- N_{012} molecules of $FeSO_4 \cdot 7H_2O$, N_{013} molecules of $H_2C_2O_4 \circ 2H_2O$, N_{014} molecules of H_2SO_4, N_{015} molecules of CO_2 and N_{016} molecules of H_2O in V_4 mL of the resulting solution

We start our considerations from the most complex dynamic system (I) $\Rightarrow$ (IV), where V mL $KMnO_4$ (C) + CO_2 (C_1) is added into V_0 mL $FeSO_4$ (C_{01}) + $H_2C_2O_4$ (C_{02}) + H_2SO_4 (C_{03}) + CO_2 (C_{04}) at the defined point of the titration. The less complex dynamic systems (I) $\Rightarrow$ (II) and (I) $\Rightarrow$ (III) will be considered later as a particular case of the system (I) $\Rightarrow$ (IV).

4.1. Formulation of GEB for the system (I) $\Rightarrow$ (IV)

Referring to the set of species in Eq. (2), we apply $a_1 = 1$ if pr1 = **FeC_2O_4** is the equilibrium solid phase (precipitate) in the system, and $a_2 = 1$ if pr2 = **MnC_2O_4** is the equilibrium solid phase in the system; otherwise, we have $a_1 = 0$ and/or $a_2 = 0$. The elemental/core balances and ChB, formulated on the basis of the set of the species Eq. (2), are as follows:

$$f_1 = f(H):$$
$$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + 2N_4n_4 + N_5(1 + 2n_5) + 2N_6n_6 + N_7(2 + 2n_7)$$
$$+ N_8(1 + 2n_8) + 2N_9n_9 + N_{10}(2 + 2n_{10}) + N_{11}(1 + 2n_{11}) + 2N_{12}n_{12} + 2N_{13}n_{13}$$
$$+ 2N_{14}n_{14} + 2N_{15}n_{15} + N_{16}(1 + 2n_{16}) + 2N_{17}n_{17} + 2N_{18}n_{18} + 2N_{19}n_{19} + 2N_{20}n_{20}$$
$$+ N_{21}(1 + 2n_{21}) + 2N_{22}n_{22} + 2N_{23}n_{23} + 2N_{24}n_{24} + 2N_{25}n_{25} + N_{26}(1 + 2n_{26}) + 2N_{27}n_{27}$$
$$+ 2N_{28}n_{28} + 2N_{29}n_{29} + 2N_{30}n_{30} + N_{31}(1 + 2n_{31}) + N_{32}(2 + 2n_{32}) + N_{33}(2 + 2n_{33})$$
$$+ 2N_{34}n_{34} + 2N_{35}n_{35} + 2N_{36}n_{36} + 2N_{37}n_{37} + 2N_{38}n_{38} + 2a_1N_{39}n_{39} + 2a_2N_{40}n_{40}$$
$$= 2N_{03} + 14N_{012} + 6N_{013} + 2N_{014} + 2N_{016}$$

$$f_2 = f(O):$$
$$N_1 + N_2n_2 + N_3(1 + n_3) + N_4n_4 + N_5(4 + n_5) + N_6(4 + n_6) + N_7(4 + n_7) + N_8(4 + n_8)$$
$$+ N_9(4 + n_9) + N_{10}(3 + n_{10}) + N_{11}(3 + n_{11}) + N_{12}(3 + n_{12}) + N_{13}(4 + n_{13}) + N_{14}(4 + n_{14})$$
$$+ N_{15}n_{15} + N_{16}(1 + n_{16}) + N_{17}(4 + n_{17}) + N_{18}(8 + n_{18}) + N_{19}(12 + n_{19}) + N_{20}n_{20}$$
$$+ N_{21}(1 + n_{21}) + N_{22}(4 + n_{22}) + N_{23}(4 + n_{23}) + N_{24}(8 + n_{24}) + N_{25}n_{25} + N_{26}(1 + n_{26})$$
$$+ N_{27}(4 + n_{27}) + N_{28}(8 + n_{28}) + N_{29}(12 + n_{29}) + N_{30}n_{30} + N_{31}(1 + n_{31}) + N_{32}(2 + n_{32})$$
$$+ N_{33}(2 + n_{33}) + N_{34}(4 + n_{34}) + N_{35}(8 + n_{35}) + N_{36}(4 + n_{36}) + N_{37}(8 + n_{37})$$
$$+ N_{38}(12 + n_{38}) + a_1N_{39}(4 + n_{39}) + a_2N_{40}(4 + n_{40}) = 4N_{01} + 2N_{02} + N_{03}$$
$$+ 11N_{012} + 6N_{013} + 4N_{014} + 2N_{015} + N_{016}$$

$$f_{12} = 2 \cdot f(O) - f(H)$$
$$-N_2 + N_3 + 7N_5 + 8N_6 + 6N_7 + 7N_8 + 8N_9 + 4N_{10} + 5N_{11} + 6N_{12} + 8N_{13} + 8N_{14} + N_{16}$$
$$+ 8N_{17} + 16N_{18} + 24N_{19}N_{21} + 8N_{22} + 8N_{23} + 16N_{24} + N_{26} + 8N_{27} + 16N_{28} + 24N_{29} + N_{31}$$
$$+ 2N_{32} + 2N_{33} + 8N_{34} + 16N_{35} + 8N_{36} + 16N_{37} + 24N_{38} + 8a_1N_{39} + 8a_2N_{40} = 8N_{01} + 4N_{02}$$
$$+ 8N_{012} + 6N_{013} + 6N_{014} + 4N_{015}$$

$$(6)$$

$f_0 = \text{ChB}$

$N_2 – N_3 + N_4 – N_5 – 2N_6 – N_8 – 2N_9 – N_{11} – 2N_{12} – N_{13} – 2N_{14} + 3N_{15} + 2N_{16} + N_{17} – N_{18} – 3N_{19}$

$+ 2N_{20} + N_{21} – 2N_{24} + 2N_{25} + N_{26} – 2N_{28} – 4N_{29} + 3N_{30} + 2N_{31} + N_{32} + 4N_{33} + N_{34}$

$– N_{35} + N_{36} – N_{37} – 3N_{38} = 0$

$$(7)$$

$–f_3 = –f(K): \qquad N_{01} = N_4 \tag{8}$

$–6f_4 = –6f(S) = –6f(SO_4): 6N_{012} + 6N_{014} = 6N_5 + 6N_6 + 6N_{22} + 6N_{27} + 6N_{34} + 12N_{35} \tag{9}$

$–4f_5 = –4f(C):$

$4N_{02} + 8N_{013} + 4N_{015} = 8N_7 + 8N_8 + 8N_9 + 4N_{10} + 4N_{11} + 4N_{12} + 8N_{17} + 16N_{18} + 24N_{19}$

$+ 8N_{23} + 16N_{24} + 16N_{28} + 24N_{29} + 8N_{36} + 16N_{37} + 24N_{38} + 8a_1N_{39} + 8a_2N_{40}$

$$(10)$$

$–3f_6 = –3f(\text{Fe}):$

$3N_{012} = 3N_{25} + 3N_{26} + 3N_{27} + 3N_{28} + 3N_{29} + 3N_{30} + 3N_{31} + 3N_{32} + 6N_{33} + 3N_{34} \tag{11}$

$+ 3N_{35} + 3N_{36} + 3N_{37} + 3N_{38} + 3a_1N_{39}$

$–2f_7 = –2f(\text{Mn}):$

$2N_{01} = 2N_{13} + 2N_{14} + 2N_{15} + 2N_{16} + 2N_{17} + 2N_{18} + 2N_{19} + 2N_{20} + 2N_{21} + 2N_{22} \tag{12}$

$+ 2N_{23} + 2N_{24} + 2a_2N_{40}$

$f_{12} + f_0 – f_3 – 6f_4 – 4f_5 – 3f_6 – 2f_7:$

$5N_{13} + 4N_{14} + N_{15} + N_{16} + N_{012} + 2N_{013} = 5N_{01} + 2N_7 + 2N_8 + 2N_9 + N_{17} + 3N_{18}$

$+ 5N_{19} + 2N_{23} + 4N_{24} + N_{25} + N_{26} + N_{27} + 5N_{28} + 7N_{29} + 2N_{36} + 4N_{37}$

$+ 6N_{38} + 3a_1N_{39} + 2a_2N_{40}$

$$(13)$$

$5[MnO_4^{-1}] + 4[MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}] – (2([H_2C_2O_4^{-1}] + [HC_2O_4^{-1}] + [C_2O_4^{-2}])$

$+ [MnC_2O_4^{+1}] + 3[Mn(C_2O_4)_2^{-1}] + 5[Mn(C_2O_4)_3^{-3}] + 2[MnC_2O_4] + 4[Mn(C_2O_4)_2^{-2}] + [Fe^{+2}]$

$+ [FeOH^{+1}] + [FeSO_4] + 5[Fe(C_2O_4)_2^{-2}] + 7[Fe(C_2O_4)_3^{-4}] + 2[FeC_2O_4^{+1}] + 4[Fe(C_2O_4)_2^{-1}]$

$+ 6[Fe(C_2O_4)_3^{-3}] + 3a_1[\mathbf{FeC_2O_4}] + 2a_2[\mathbf{MnC_2O_4}]) = 5CV/(V_0 + V)$

$– (C_{01} + 2C_{02})V_0/(V_0 + V) \Rightarrow$

$2([H_2C_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) + [MnC_2O_4^{+1}] + 3[Mn(C_2O_4)_2^{-1}] + 5[Mn(C_2O_4)_3^{-3}]$

$+ 2[MnC_2O_4] + 4[Mn(C_2O_4)_2^{-2}] + [Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] + 5[Fe(C_2O_4)_2^{-2}]$

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

$+ 2a_2[\mathbf{MnC_2O_4}] – (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}])$

$= ((C_{01} + 2C_{02})V_0 – 5CV)/(V_0 + V)$

$$(14)$$

Eq. (14) is the shortest/simplest form of GEB for the related system; it is, of course, different from the identity 0 = 0. On the basis of Eq. (14), one can also formulate the GEB for the system (I) $\Rightarrow$ (II):

$$(KMnO_4(C) + CO_2(C_1), V) \Rightarrow (FeSO_4(C_{01}) + H_2SO_4(C_{03}) + CO_2(C_{04}), V_0) \qquad (15)$$

and for the system (I) $\Rightarrow$ (III):

$$(KMnO_4(C) + CO_2(C_1), V) \Rightarrow (H_2C_2O_4(C_{02}) + H_2SO_4(C_{03}) + CO_2(C_{04}), V_0) \qquad (16)$$

Assuming C_{02} = 0, after omission of the related species involved with oxalates, from Eq. (14), we have the GEB valid for the system (I) $\Rightarrow$ (II):

$$\begin{aligned} &[Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] - (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}]) \\ &= (C_{01}V_0 - 5CV)(V_0 + V) \end{aligned} \qquad (17)$$

Assuming C_{01} = 0, after omission of the related Fe-species, from Eq. (14), we have the GEB valid for the system (I) $\Rightarrow$ (III)

$$\begin{aligned} &2([H_2O_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) + [MnC_2O_4^{+1}] + 3[Mn(C_2O_4)_2^{-1}] + 5[Mn(C_2O_4)_3^{-3}] \\ &+ 2[MnC_2O_4] + 4[Mn(C_2O_4)_2^{-2}] + 2a_2[\mathbf{MnC_2O_4}] - (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + [Mn^{+3}] \\ &+ [MnOH^{+2}]) = (2C_{02}V_0 - 5CV)(V_0 + V) \end{aligned} \qquad (18)$$

On the other hand, Eqs. (17) and (18) are the simplest/shortest linear combinations for the related subsystems of the system (I) $\Rightarrow$ (IV); both are also different from the identity, of course. For comparison, the linear combination $f_{12} + f_0 - f_3 - 6f_4 - 4f_5 - 2f_6 - 2f_7 = 0$, that is where $-2f_6$ is put for $-3f_6$, gives a more extended equation, where more components are involved. Anyway, we get here the equation, not the identity 0 = 0. It must be stressed that none of the linear combinations of these equations gives the identity. This is the general property of all redox systems, of any degree of complexity.

5. Confirmation of linear dependency of balances for non-redox systems

It can be stated that $2f(O) - f(H)$ is a linear combination of charge and elemental/core balances for non-redox systems of any degree of complexity; this means that $2f(O) - f(H)$ is not a new, independent balance in non-redox systems. From Eq. (4), we see that for non-redox systems, f_{12} can be expressed as the linear combination of other balances of the system considered:

$$\begin{aligned} &(I) f_{12} = f_3 + 7f_4 + 4f_5 - f_0; \qquad (II) f_{12} = 2f_3 + 6f_4 + 4f_5 - f_0; \\ &(III) f_{12} = 6f_3 + 4f_4 + 6f_5 - f_0; \quad (IV) f_{12} = 6f_3 + 4f_4 + 6f_5 + 2f_6 - f_0 \end{aligned} \qquad (19)$$

Eq. (4) can be also rewritten into equivalent forms:

$$
\begin{aligned}
&(I).... \ (+1)f_1 + (-2)\cdot f_2 + (+1)f_3 + (+7)f_4 + (+4)\cdot f_5 - f_0 = 0; \\
&(II)(+1)\cdot f_1 + (-2)\cdot f_2 + (+2)\cdot f_3 + (+6)\cdot f_4 + (+4)\cdot f_5 - f_0 = 0; \\
&(III)(+1)\cdot f_1 + (-2)\cdot f_2 + 2(+3)\cdot f_3 + (+4)\cdot f_4 + (+6)\cdot f_5 - f_0 = 0; \\
&(IV)(+1)\cdot f_1 + (-2)\cdot f_2 + (+2)\cdot f_6 + 2(+3)\cdot f_3 + (+4)\cdot f_4 + (+6)\cdot f_5 - f_0 = 0
\end{aligned}
\tag{20}
$$

As we see, the coefficient at the corresponding elemental/core balance in the related sum is equal to the oxidation number of the corresponding element. The linear dependence will be thus ascertained by multiplying the elemental/core balances by the appropriate oxidation numbers. After consecutive addition of the resulting balances to the sum of $2f$(O)–f(H) and charge balance, followed by simplifications, the resulting sum is reduced to the identity 0 = 0. It is the simplest way of checking the linear dependency of the equations related to non-redox systems.

For redox systems, the appropriate linear combination of $2f$(O)–f(H) with charge balance and elemental/core balances related to electron-non-active elements in the system in question leads to the simplest form of GEB named as generalized electron balance (GEB). It means that the GEB is a new balance, complementary/compatible with other (charge and elemental/core) balances related to the system in question.

6. Confirmation of linear independency of balances for redox systems

Applying a similar procedure, one can also state that $2f$(O)–f(H) is not a linear combination of charge and elemental/core balances for redox systems of any degree of complexity; it means that $2f$(O)–f(H) is a new/independent balance in redox systems.

The independency/dependency property of the balance $2f$(O)–f(H) is the basis for the division of electrolytic systems into redox and non-redox systems [8, 9]. This rule is illustrated by the following examples, related to static and dynamic systems.

7. Confirmation of equivalency of approaches I and II to GEB for the system (I) ⇒ (IV)

We apply now the linear combination (algebraic sum) of Eqs. (6–9) for ChB and elemental/core balances, involving electron-non-active elements: H, O, K and S, perceived in terms of the Approach I to GEB as 'fans', we have:

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

$$6N_7 + 6N_8 + 6N_9 + 4N_{10} + 4N_{11} + 4N_{12} + 7N_{13} + 6N_{14} + 3N_{15} + 3N_{16} + 9N_{17} + 15N_{18}$$
$$+ 21N_{19} + 2N_{20} + 2N_{21} + 2N_{22} + 8N_{23} + 14N_{24} + 2N_{25} + 2N_{26} + 2N_{27} + 14N_{28} + 20N_{29}$$
$$+ 3N_{30} + 3N_{31} + 3N_{32} + 6N_{33} + 3N_{34} + 3N_{35} + 9N_{36} + 15N_{37} + 21N_{38} + 8a_1N_{39} + 8a_2N_{40}$$
$$= 7N_{01} + 6N_{013} + 4(N_{02} + N_{015}) \Rightarrow 6(N_7 + N_8 + N_9) + 4(N_{10} + N_{11} + N_{12}) + 7N_{13} + 6N_{14}$$
$$+ 3N_{15} + 3N_{16} + 9N_{17} + 15N_{18} + 21N_{19} + 2(N_{20} + N_{21} + N_{22}) + 8N_{23} + 14N_{24}$$
$$+ 2(N_{25} + N_{26} + N_{27}) + 14N_{28} + 20N_{29} + 3(N30 + N31 + N32 + 2N33 + N_{34} + N_{35})$$
$$+ 9N_{36} + 15N_{37} + 21N_{38} + 8a_1N_{39} + 8a_2N_{40} = 7N_{01} + 6N_{013} + 4(N_{02} + N_{015})$$

$$(21)$$

Denoting by Z_C (= 6), Z_{Fe} (= 26) and Z_{Mn} (= 25), the atomic numbers for electron-active elements ('players') C, Fe and Mn, from Eqs. (10)–(12) and (21), we have, by turns,

$$Z_C \cdot f_5 + Z_{Fe} \cdot f_6 + Z_{Mn} \cdot f_7 - (f_{12} + f_0 - f_3 - 6f_4)$$
$$(2Z_C - 6)(N_7 + N_8 + N_9) + (Z_C - 4)(N_{10} + N_{11} + N_{12}) + (Z_{Mn} - 7)N_{13} + (Z_{Mn} - 6)N_{14}$$
$$+ (Z_{Mn} - 3)(N_{15} + N_{16}) + N_{17}(Z_{Mn} + 2Z_C - 9) + N_{18}(Z_{Mn} + 4Z_C - 15) + N_{19}(Z_{Mn} + 6Z_C - 21)$$
$$+ (Z_{Mn} - 2)(N_{20} + N_{21} + N_{22}) + N_{23}(Z_{Mn} + 2Z_C - 8) + N_{24}(Z_{Mn} + 4Z_C - 14) + (Z_{Fe} - 2)(N_{25}$$
$$+ N_{26} + N_{27})(Z_{Fe} + 4Z_C - 12)N_{28} + (Z_{Fe} + 6Z_C - 20)N_{29} + (Z_{Fe} - 3)(N_{30} + N_{31} + N_{32})$$
$$+ 2(Z_{Fe} - 3)N_{33} + (Z_{Fe} - 3)(N_{34} + N_{35})(Z_{Fe} + 2Z_C - 9)N_{36} + (Z_{Fe} + 4Z_C - 15)N_{37}$$
$$+ (Z_{Fe} + 6Z_C - 21)N_{38} + a_1(Z_{Fe} + 2Z_C - 8)N_{39} + a_2(Z_{Mn} + 2Z_C - 8)N_{40} = (Z_{Mn} - 7)N_{01}$$
$$+ (Z_{Fe} - 2)N_{012} + 2(Z_C - 3)N_{013} + (Z_C - 4)(N_{02} + N_{015})$$

$$2(Z_C - 3)(N_7 + N_8 + N_9) + (Z_C - 4)(N_{10} + N_{11} + N_{12}) + (Z_{Mn} - 7)N_{13} + (Z_{Mn} - 6)N_{14}$$
$$+ (Z_{Mn} - 3)(N_{15} + N_{16}) + N_{17}(Z_{Mn} + 2Z_C - 9) + N_{18}(Z_{Mn} + 4Z_C - 15) + N_{19}(Z_{Mn} + 6Z_C - 21)$$
$$+ (Z_{Mn} - 2)(N_{20} + N_{21} + N_{22}) + N_{23}(Z_{Mn} + 2Z_C - 8) + N_{24}(Z_{Mn} + 4Z_C - 14) + (Z_{Fe} - 2)(N_{25}$$
$$+ N_{26} + N_{27})(Z_{Fe} + 4Z_C - 12)N_{28} + (Z_{Fe} + 6Z_C - 20)N_{29} + (Z_{Fe} - 3)(N_{30} + N_{31} + N_{32})$$
$$+ 2(Z_{Fe} - 3)N_{33} + (Z_{Fe} - 3)(N_{34} + N_{35})(Z_{Fe} + 2Z_C - 9)N_{36} + (Z_{Fe} + 4Z_C - 15)N_{37}$$
$$+ (Z_{Fe} + 6Z_C - 21)N_{38} + a_1(Z_{Fe} + 2Z_C - 8)N_{39} + a_2(Z_{Mn} + 2Z_C - 8)N_{40}$$
$$= (Z_{Mn} - 7)N_{01} + (Z_{Fe} - 2)N_{012} + 2(Z_C - 3)N_{013} + (Z_C - 4)(N_{02} + N_{015})$$

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

$$(22)$$

Eq. (22) is obtainable immediately according to the Approach I to GEB [19–22]. Note, for example, that:

$$N_{17}(Z_{Mn} + 2Z_C - 9) = N_{17}(Z_{Mn} - 3 + 1°2 \cdot (Z_C - 3))$$
$$N_{18}(Z_{Mn} + 4Z_C - 15) = N_{18}(Z_{Mn} - 3 + 2°2 \cdot (Z_C - 3))$$
$$N_{19}(Z_{Mn} + 6Z_C - 21) = N_{19}(Z_{Mn} - 3 + 3°2 \cdot (Z_C - 3)$$

The equation for GEB thus obtained (according to the Approach II to GEB [1, 4, 7–18, 24, 25]) is then equivalent to GEB, obtained according to the Approach I to GEB, based on the principle of the common pool of electrons introduced by electron-active elements ('players') of the system in question. For redox systems, the GEB is the inherent part of the generalized approach to electrolytic systems (GATES) [1], denoted as GATES/GEB.

8. Some generalizing remarks on GEB

The linear combination 2*f*(O)−*f*(H) of elemental balances, *f*(H) for H and *f*(O) for O, is a keystone of the overall thermodynamic knowledge on electrolytic systems. The 2*f*(O) −*f*(H) can be formulated both for non-redox and redox systems, with amphiprotic (co)solvent(s) involved. It is the basis for the Generalized Electron Balance (GEB) formulated according to the Approach II to GEB.

The principle of GEB formulation was presented for the first time in Refs. [30, 31] and then in Refs. [19–22, 31–36] as the Approach I to GEB. The GEB formulation according to the Approach I is based on the 'card game' principle, with a common pool of electrons as money, electron-active elements as players and electron-non-active elements as fans—not changing their oxidation degree, that is the fans' accounts are intact in this convention [13, 23], see an illustration below. Electrons are considered as money, transferred between players; the knowledge of oxidation numbers of all elements in the system in question is needed there.

The Approach I to GEB, named also as the 'short' version of GEB, needs a knowledge of oxidation numbers for all elements in the species participating in the system that is considered. The equivalency of the Approaches I and II means that the equation obtained by a suitable linear combination of pr-GEB with charge balance and other elemental/core balances becomes identical with the one obtained directly from the Approach I to GEB.

Although derivation of GEB according to the Approach II is more extensive/laborious, it enables to formulate this balance without prior knowledge of oxidation numbers for the elements involved in the system. It is the paramount advantage of the Approach II to GEB, particularly when applied to more complex organic species, with radicals and ion-radicals involved. Moreover, within the Approaches I and II, the roles of oxidants and reducers are not ascribed a priori to particular components forming the redox system and the species formed in this system.

Ultimately, GEB, charge and elemental/core balances are expressed in terms of molar concentrations—to be fully compatible with expressions for equilibrium constants, interrelating

molar concentrations of defined species on the basis of the mass action law applied to the correctly written reaction equation. The law of mass action is the one and only chemical law applied in GATES.

GEB is perceived as the law of matter conservation, as the general law of nature related to electrolytic (aqueous, non-aqueous or mixed-solvent media) redox systems and as a synthesis of physical and chemical laws [1, 14, 15, 23, 24, 27]. This law can also be extended on the systems with mixed (e.g., binary) solvents with amphiprotic (protophilic and protogenic) and aprotic properties. GEB is a rather unexpected consequence of the concentration balances for H and O, and therefore the formulation of GEB, especially as the Approach II to GEB, is regarded as the scientific discovery and not as a confirmation of the obvious fact arising from other, fundamental laws of nature. This fact is emphasized in this chapter in the context of philosophical understanding of the scientific discoveries in the aspect of the laws of nature.

The GEB, together with charge and concentration/core balances and a set of independent equilibrium constants, provides a complete set of equations used for a thermodynamic description of a redox system taken for quantitative considerations within GATES/GEB $\in$ GATES.

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.

The Approach II to GEB shows that the equivalent equations for GEB are derived from the common root of the elements conservation and then GEB is fully compatible with charge and concentration balances like 'the lotus flower, lotus leaf and lotus seed come from the same root' [13]. This compatibility is directly visible from the viewpoint of the Approach II to GEB. The GEB, based on a reliable law of the matter conservation, is equally robust as equations for charge and concentration balances. The complementarity of the GEB (Approaches I and II) to other balances is regarded as the expression of harmony of nature, and GATES/GEB is an example of excellent epistemological paradigm [27].

The number of electron-active elements (considered as players, in terms of Approach I to GEB) in a redox system, considered according to GATES/GEB principles, is practically unlimited; among others, the systems with three [24] or four [1] players were considered.

In the modeling of real systems, it is assumed that an effect of the matter (such as H_2O, CO_2 and O_2) exchange with the environment is negligibly small within the period designed for certain chemical operations made on the system.

9. Completion of balances

The set of balances for the system (I) $\Rightarrow$ (IV) is composed of GEB (e.g., 14 or 22) and equations obtained from the balances (7)–(12) are expressed in terms of molar concentrations, namely:

$[H^{+1}] - [OH^{-1}] + [K^{+1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] - [HC_2O_4^{-1}] - 2[C_2O_4^{-2}] - [HCO_3^{-1}] - 2[CO_3^{-2}] - [MnO_4^{-1}]$
$-2[MnO_4^{-2}] + 3[Mn^{+3}] + 2[MnOH^{+2}] + [MnC_2O_4^{+1}] - [Mn(C_2O_4)_2^{-1}] - 3[Mn(C_2O_4)_3^{-3}] + 2[Mn^{+2}]$
$+ [MnOH^{+1}] - 2[Mn(C_2O_4)_2^{-2}] + 2[Fe^{+2}] + [FeOH^{+1}] - 2[Fe(C_2O_4)_2^{-2}] - 4[Fe(C_2O_4)_3^{-4}] + 3[Fe^{+3}]$
$+ 2[FeOH^{+2}] + [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] - [Fe(SO_4)_2^{-1}] + [FeC_2O_4^{+1}]$
$-[Fe(C_2O_4)_2^{-1}] - 3[Fe(C_2O_4)_3^{-3}] = 0$

$$\tag{23}$$

$$[K^{+1}] = CV/(V_0 + V) \tag{24}$$

CB(S) :
$$[HSO_4^{-1}] + [SO_4^{-2}] + [MnSO_4] + [FeSO_4] + [FeSO_4^{+1}] + 2[Fe(SO_4)_2^{-1}] = (C_{01} + C_{03})V_0/(V_0 + V)$$

$$\tag{25}$$

CB(C) :
$2([H_2C_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) + [H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}]$
$+2[MnC_2O_4] + 4[Mn(_{C_2O_4)2}^{-2}] + 4[Fe(C_2O_4)2^{-2}] + 6[Fe(C_2O_4)_3^{-4}] + 2[FeC_2O_4^{+1}]$
$+4[Fe(C_2O_4)_2^{-1}] + 6[Fe(C_2O_4)_3^{-3}] + 2a_1[\mathbf{FeC_2O_4}] + 2a_2[\mathbf{MnC_2O_4}]$
$= ((2C_{02} + C_{04})V_0 + C_1V)/(V_0 + V)$

$$\tag{26}$$

CB(Fe) :
$[Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] + [Fe(_{C_2O_4)2}^{-2}] + [Fe(_{C_2O_4)3}^{-4}] + [Fe^{+3}] + [FeOH^{+2}]$
$+[Fe(_{OH)2}^{+1}] + 2[Fe_2(_{OH)2}^{+4}] + [FeSO_4^{+1}] + [Fe(_{SO_4)2}^{-1}] + [FeC_2O_4^{+1}] + [Fe(C_2O_4)2^{-1}]$
$+[Fe(C_2O_4)3^{-3}] + a_1[\mathbf{FeC_2O_4}] = C_{01}V_0/(V_0 + V)$

$$\tag{27}$$

CB(Mn) :
$[MnO_4^{-1}] + [MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}] + [MnC_2O_4^{+1}] + [Mn(C_2O_4)2^{-1}]$
$+[Mn(C_2O_4)3^{-3}] + [Mn^{+2}] + [MnOH^{+1}] + [MnSO_4] + [MnC_2O_4] + [Mn(C_2O_4)2^{-2}]$
$+a_2[\mathbf{MnC_2O_4}] = CV/(V_0 + V)$

$$\tag{28}$$

The balances can be specified as equations or equalities. The equality is represented here by relation (24), where only one species is involved. In Eqs. (23) and (25)–(28), we have concentrations of more species, interrelated in expressions for equilibrium constants, formulated on the basis of the proper stoichiometric reaction notations. As with above results, we have seven balances: six equations and one equality for the system (I) ⇒ (IV); the equality (24) can enter immediately the charge balance (23). The current volume V of titrant T added is a parameter (steering variable) in these balances.

10. The arrangement of relations for equilibrium constants

The balances written in terms of molar concentrations are congruent with a complete set of independent (non-contradictory [9, 16]) relations for the equilibrium constants, interrelating concentrations of some species in the balances.

The complete set of equilibrium constants, namely ionic product of water, dissociation constants, standard potentials, stability constants of complexes and interrelated concentrations of the species (except K^{+1}) is presented in Eq. (2).

$\{1\}[H^{+1}][OH^{-1}] = 10^{-14}$; $\{2\}[HSO_4^{-1}] = 10^{1.8}[H^{+1}][SO_4^{-2}]$; $\{3\}[H_2C_2O_4] = 10^{5.2}[H^{+1}][C_2O_4^{-2}]$; $\{4\}[HC_2O_4^{-1}] = 10^{3.8}[H^{+1}][C_2O_4^{-2}]$;

$\{5\}[H_2CO_3] = 10^{16.4}[H^{+1}]^2[CO_3^{-2}]$; $\{6\}[HCO_3^{-1}] = 10^{10.1}[H^{+1}][CO_3^{-2}]$; $\{7\}[H_2CO_3] = [H_2C_2O_4^{0.5°}10^{A(E+0.396)+pH}$;

$\{8\}[MnO_4^{-1}] = [Mn^{+2}] \cdot 10^{5A(E-1.507)+8pH}$; $\{9\}[MnO_4^{-2}] = [Mn^{+2}] \cdot 10^{4A(E-1.743)+8pH}$; $\{10\}[Mn^{+3}] = [Mn^{+2}] \cdot 10^{A(1.509)}$;

$[11][Fe^{+3}] = [Fe^{+2}] \cdot 10^{A(E-0.771)}$; $\{12\}[FeOH^{+1}] = 10^{4.5}[Fe^{+2}][OH^{-1}]$; $\{13\}[FeSO_4] = 10^{2.3}[Fe^{+2}][SO_4^{-2}]$;

$\{14\}[Fe(C_2O_4)2^{-2}] = 10^{4.52}[Fe^{+2}][C_2O_4^{-2}]^2$; $\{15\}[Fe(C_2O_4)3^{-4}] = 10^{5.22}[Fe^{+2}][C_2O_4^{-2}]^3$; $\{16\}[FeOH^{+2}] = 10^{11.0}[Fe^{+3}][OH^1]$;

$\{17\}[Fe(_{OH)2}^{+1}] = 10^{21.7}[Fe^{+3}][^{OH^{-1}]2}$; $\{18\}[Fe_2(_{OH)2}^{+4}] = 10^{25.1}[^{Fe^{+3}]2}[^{OH^{-1}]2}$; $\{19\}[FeSO_4^{+1}] = 10^{4.18}[Fe^{+3}][SO_4^{-2}]$;

$\{20\}[Fe(_{SO_4)2}^{-1}] = 10^{7.4}[Fe^{+3}][SO_4^{-2}]^2$; $\{21\}[FeC_2O_4^{+1}] = 10^{7.53}[Fe^{+3}][C_2O_4^{-2}]$; $\{22\}[Fe(C_2O_4)2^{-1}] = 10^{13.64}[Fe^{+3}][C_2O_4^{-2}]^2$;

$\{23\}[Fe(C_2O_4)3^{-3}] = 10^{18.46}[Fe^{+3}][C_2O_4^{-2}]^3$; $\{24\}[MnOH^{+1}] = 10^{3.4}[Mn^{+2}][OH^{-1}]$; $\{25\}[MnSO_4]$

$\{26\}[MnC_2O_4] = 10^{3.82}[Mn^{+2}][C_2O_4^{-2}]$; $\{27\}[Mn(C_2O_4)2^{-2}] = 10^{5.25}[Mn^{+2}][C_2O_4^{-2}]^2$; $\{28\}[MnOH^{+2}] = 10^{14.2}[Mn^{+3}][OH^{-1}]$;

$\{29\}[MnC_2O_4^{+1}] = 10^{9.98}[Mn^{+3}][C_2O_4^{-2}]$; $\{30\}[Mn(C_2O_4)2^{-1}] = 10^{16.57}[Mn^{+3}][C_2O_4^{-2}]^2$; $\{31\}[Mn(C_2O_4)3^{-3}]$

$\{32\}[Fe^{+2}][C_2O_4^{-2}] = 10^{-6.7}$ for pr1 = **FeC$_2$O$_4$** and $\}7B33 \}7D[Mn^{+2}][C_2O_4^{-2}] = 10^{-5.3}$ for pr2 = **MnC$_2$O$_4$**

$$(29)$$

11. Relation between the numbers of species, balances and equilibrium constants

For any electrolytic system, one can define the relationship between the numbers of (i) kinds of species (P) (with free H_2O molecules included), (ii) independent balances (Q) and (iii) independent equilibrium constant (R) values.

We refer first to non-redox systems discussed in Section 3, and we have:

- for the system I: P = 8, Q = 4 (from f_0, f_3, f_4, f_5) and R = 3 ({1,5,6})

- for the system II: P = 11, Q = 4 (from f_0, f_3, f_4, f_5) and R = 6 ({1,2,5,6,12,13})

- for the system III: P = 11, Q = 4 (from f_0, f_3, f_4, f_5) and R = 6 ({1–6})

- for the system IV: P = 17, Q = 5 (from f_0, f_3, f_4, f_5, f_6) and R = 11 ({1--6,12–15,32})

Referring now to the redox systems, we have:

- for the system (I) $\Rightarrow$ (II): P = 25, Q = 7 (GEB,ChB,CB(K),CB(CO_3),CB(S),CB(Fe),CB(Mn)) and R = 18 ({1,2,3,4,5,6,12,13,14,15,32})

- for the system (I) $\Rightarrow$ (III): P = 25, Q = 6 (GEB,ChB,CB(K),CB(C),CB(S),CB(Mn)) and R = 19 ({1–10,24–31,33})

- for the system (I) $\Rightarrow$ (IV): P = 40 (collected in 2), Q = 7 (GEB,ChB,CB(K),CB(C),CB(S),CB(Fe),CB(Mn)) and R = 33 (collected in 29)

On this basis, one can state the relationships:

- P = Q + R + 1—for non-redox systems;

- P = Q + R—for redox systems.

To standardize this relationship, it is (informally) assumed that the electron is one of the species in the redox systems. In this way, the number of species is increased by 1, and we can suggest the relationship

$$P = Q + R + 1 \tag{30}$$

as common for both redox and non-redox electrolytic systems, regardless of their degree of complexity. The relation (30), applicable in resolution of electrolytic systems, was first presented in Ref. [37]; it can be perceived as a useful counterpart of the Gibbs' phase rule (of a similar 'degree of complexity') in this area of the knowledge.

It should be noted that the total number, P = 40, of kinds of species involved in the system (I) $\Rightarrow$ (IV) is relatively high.

12. The steps realized within GATES/GEB

Modeling the electrolytic systems according to GATES/GEB consists of several interacting steps [1]: (1) collection of preliminary data; (2) preparation of computer programs; (3) calculations and data handling and (4) knowledge gaining; all the steps are indicated in **Figure 1**.

12.1. Collection of preliminary data

The necessary physicochemical knowledge is mainly attainable in tables of physicochemical data, exemplified by monographs [38–40]. It should be noted that the period of interest in this
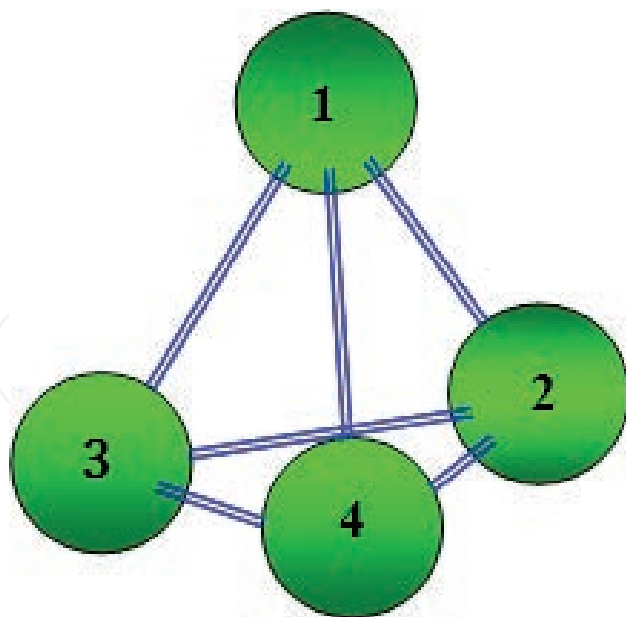
Figure 1. The steps of modeling any electrolytic system [1].

field of research is currently the past. On the other hand, the physicochemical constants originate from works released over several decades, which are clearly seen in Ref. [40], where the relevant information is included. The point is that these physicochemical constants were determined using models that had been adapted to current computing capabilities, especially in the pre-computer era; these calculations were based (exclusively, in principle) on the reaction stoichiometry. For example, the solubility products were determined on the basis of molar solubility, see for example, the remark in Refs. [41, 42], without checking whether the precipitate is the equilibrium solid phase in the system [43–48]. Acid dissociation constants were mainly determined on the basis of the Ostwald's formula (see e.g., [49, 50]). Conditional ('formal', not normal) potentials were determined for many redox pairs [51]. In the computer era, some new models resolved with use of iterative methods were elaborated. The assumptions and implementation of these models in relevant experimental studies aroused a number of concerns expressed, among others, in Refs. [52, 53]. Despite these circumstances, GATES and GATES/GEB, in particular, provides a new and reliable tool, applicable for physicochemical knowledge gaining. Thanks to this tool, it will be possible, in the immediate future, for a renaissance of interest in this—so important, after all!—field of fundamental research, which cannot be creatively developed on the basis of the previous 'paradigm' [27] based on the stoichiometry concept.

12.2. Preparation of computer program

Modeling of electrolytic systems can be realized with the use of iterative computer programs, for example MATLAB, perceived as a universal and high-level programming language [54, 55]. From the viewpoint of the form of mathematical models, MATLAB is focused on the matrix algebra procedure. MATLAB allows to make a quick and accurate computation and visualization of numerical data.

The iterative computer programs, written in MATLAB language, are exemplified in Refs. [11, 12, 16].

12.3. Calculations and data handling

The calculations can be made at different levels of the preliminary, physicochemical knowledge about the system in question. What is more, some 'variations on the subject' can also be done for this purpose; it particularly refers to metastable and non-equilibrium systems. A special emphasis will be put on complex redox systems, where all types of elementary chemical reactions proceed simultaneously and/or sequentially. In all instances, one can follow measurable quantities (potential E, pH) in dynamic and static processes and gain the information about many details not measurable in real experiments; it particularly refers to dynamic speciation.

We refer here to dynamic (titration) redox systems, represented by the system of $2 + k$ nonlinear equations composed of GEB, charge balance and k (≥ 1) concentration balances. The results of calculations, made with the use of an iterative computer program, are presented graphically. Thus, the plots $E = E(\Phi)$ and $pH = pH(\Phi)$ for potential E and pH of the solution and $\log[X_i^{z_i}]$ versus Φ (Eq. (5)) relationships (speciation curves) will be drawn.

The Φ concept is used for simpler systems, providing a kind of normalization (independence on V_0) in the systems considered. Φ plays a key role in the formulation of the generalized equivalence mass (GEM) concept, introduced also by Michałowski [25]. In more complex systems, the volume V is put on the abscissa.

The numerical data can be visualized in the form of two- or three-dimensional graphs (2*D*, 3*D*), see for example Ref. [12].

12.4. Computer program for the system (I) $\Rightarrow$ (III)

The set of independent equilibrium constants is involved in the algorithm needed for calculation purposes [14], realized in the system (I) $\Rightarrow$ (IV) as specified above. An algorithm is a well-defined procedure, expressed by a sequence of unambiguous instructions, which allows a computer to solve a problem according to a computer program implemented for this purpose. The term 'unambiguous' indicates that there is no room for subjective interpretation.

The system (I) $\Rightarrow$ (IV) and its subsystems (I) $\Rightarrow$ (II) and (I) $\Rightarrow$ (III) were simulated using an iterative computer program (MATLAB software, included in the optimization toolbox™). In particular, the computer program for the system (I) $\Rightarrow$ (III) is as follows.

function F = Function_KMnO4_Na2C2O4(x)

global V Vmin Vstep Vmax V0 C C1 C0 C01 C02 fi H OH pH E Kw pKw A aa

global H2C2O4 HC2O4 C2O4 H2CO3 HCO3 CO3 K

global logH2C2O4 logHC2O4 logC2O4 logH2CO3 logHCO3 logCO3 logK

```
global Mn7O4 Mn6O4 HSO4 SO4 Na

global logMn7O4 logMn6O4 logHSO4 logSO4 logNa

global Mn3 Mn3OH Mn3C2O4 Mn3C2O42 Mn3C2O43

global logMn3 logMn3OH logMn3C2O4 logMn3C2O42 logMn3C2O43

global Mn2 Mn2OH Mn2SO4 Mn2C2O4 Mn2C2O42

global logMn2 logMn2OH logMn2SO4 logMn2C2O4 logMn2C2O42

global pr logpr q logq

pH=x(1);

E=x(2);

if aa==0

    Mn2=10.^-x(3);

    pr=0;

else

    pr=10.^-x(3);

end;

H2C2O4=10.^-x(4);

SO4=10.^-x(5);

H=10.^-pH;

pKw=14;

Kw=10.^-14;

OH=Kw./H;

A=16.92;

ZMn=25;

ZC=6;

Ksp=10.^-5.3;

HC2O4=10.^(pH-1.25).*H2C2O4;

C2O4=10.^(pH-4.27).*HC2O4;

H2CO3=10.^(A.*(E+0.386)).*H2C2O4.^0.5;

HCO3=10.^(pH-6.3).*H2CO3;
```

CO3=10.^(pH-10.1).*HCO3;

if aa==1

  Mn2=Ksp./C2O4;

end;

HSO4=10.^(1.8-pH).*SO4;

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

Mn6O4=10.^(A.*(0.56-E)).*Mn7O4;

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

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

Mn2C2O4=10.^3.82.*Mn2.*C2O4;

Mn2C2O42=10.^5.25.*Mn2.*C2O4.^2;

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

Mn3OH=10.^(pH-0.2).*Mn3;

Mn3C2O4=10.^9.98.*Mn3.*C2O4;

Mn3C2O42=10.^16.57.*Mn3.*C2O4.^2;

Mn3C2O43=10.^19.42.*Mn3.*C2O4.^3;

K=C.*V./(V0+V);

Na=C0.*V0./(V0+V);

  %Charge balance

F=[(H-OH+K+Na-HSO4-2.*SO4-HC2O4-2.*C2O4-HCO3-2.*CO3-Mn7O4-2.*Mn6O4…

  +3.*Mn3+2.*Mn3OH+Mn3C2O4-Mn3C2O42-3.*Mn3C2O43+2.*Mn2+Mn2OH…

  -2.*Mn2C2O42);

  %Concentration balance of Mn

  (Mn7O4+Mn6O4+Mn3+Mn3OH+Mn3C2O4+Mn3C2O42+Mn3C2O43…

  +Mn2+Mn2OH+Mn2SO4+Mn2C2O4+Mn2C2O42+aa.*pr-C.*V./(V0+V));

  %Concentration balance of C

  (2.*H2C2O4+2.*HC2O4+2.*C2O4+H2CO3+HCO3+CO3+2.*Mn2C2O4…

  +4.*Mn2C2O42+2.*Mn3C2O4+4.*Mn3C2O42+6.*Mn3C2O43…

+2.*aa.*pr-(2.*C0.*V0+C02.*V0+C1.*V)./(V0+V));

%Concentration balance of S

(HSO4+SO4+Mn2SO4-C01.*V0./(V0+V));

%Electron balance

((ZMn-7).*Mn7O4+(ZMn-6).*Mn6O4+(ZMn-3).*(Mn3+Mn3OH)…

+(ZMn-2).*(Mn2+Mn2OH+Mn2SO4)+(ZC-4).*(H2CO3+HCO3+CO3)…

+2.*(ZC-3).*(H2C2O4+HC2O4+C2O4)+(ZMn-3+2.*ZC-6).*Mn3C2O4…

+(ZMn-3+4.*ZC-12).*Mn3C2O42+(ZMn-3+6.*ZC-18).*Mn3C2O43…

+(ZMn-2+2.*ZC-6).*Mn2C2O4+(ZMn-2+4.*ZC-12).*Mn2C2O42+…

+(ZMn-2+2.*ZC-6).*aa.*pr…

-((2.*ZC-6).*C0.*V0+(ZC-4).*C02.*V0+(ZC-4).*C1.*V…

+(ZMn-7).*C.*V)./(V0+V))];

q=Mn2.*C2O4./Ksp;

logMn2=log10(Mn2);

logMn2OH=log10(Mn2OH);

logMn2SO4=log10(Mn2SO4);

logq=log10(q);

logpr=log10(pr);

logMn2C2O4=log10(Mn2C2O4);

logMn2C2O42=log10(Mn2C2O42);

logMn3=log10(Mn3);

logMn3OH=log10(Mn3OH);

logMn3C2O4=log10(Mn3C2O4);

logMn3C2O42=log10(Mn3C2O42);

logMn3C2O43=log10(Mn3C2O43);

logMn6O4=log10(Mn6O4);

logMn7O4=log10(Mn7O4);

logH2CO3=log10(H2CO3);

logHCO3=log10(HCO3);

logCO3=log10(CO3);

logH2C2O4=log10(H2C2O4);

logHC2O4=log10(HC2O4);

logC2O4=log10(C2O4);

logHSO4=log10(HSO4);

logSO4=log10(SO4);

logNa=log10(Na);

logK=log10(K);

%The end of program

13. Graphical presentation of the data

The results of calculations in the system (I) ⇒ (IV) are presented in **Figures 2–4**. More detailed, numerical data are specified in Ref. [14].
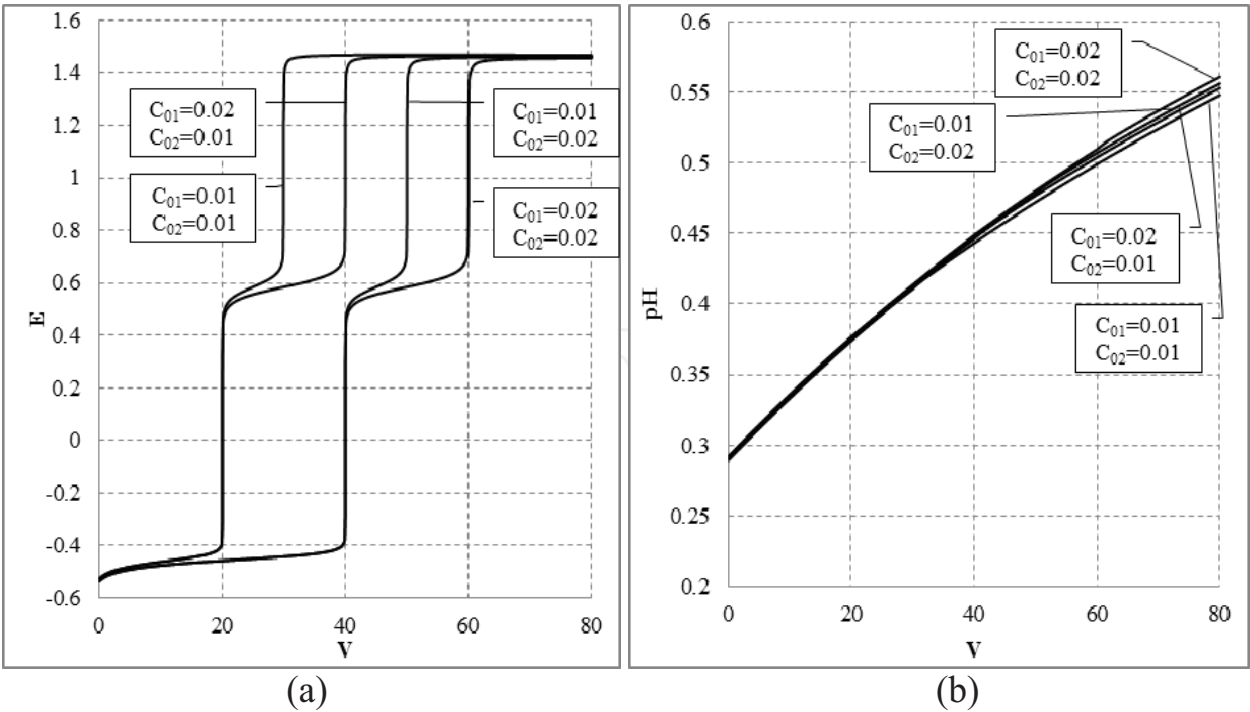

Figure 2. The (a) E versus V and (b) pH versus V relationships plotted at $V_0 = 100$, $C = 0.02$, $C_{03} = 0.5$, $C_1 = C_{04} = 0.001$ and indicated pairs of C_{01} and C_{02} values.
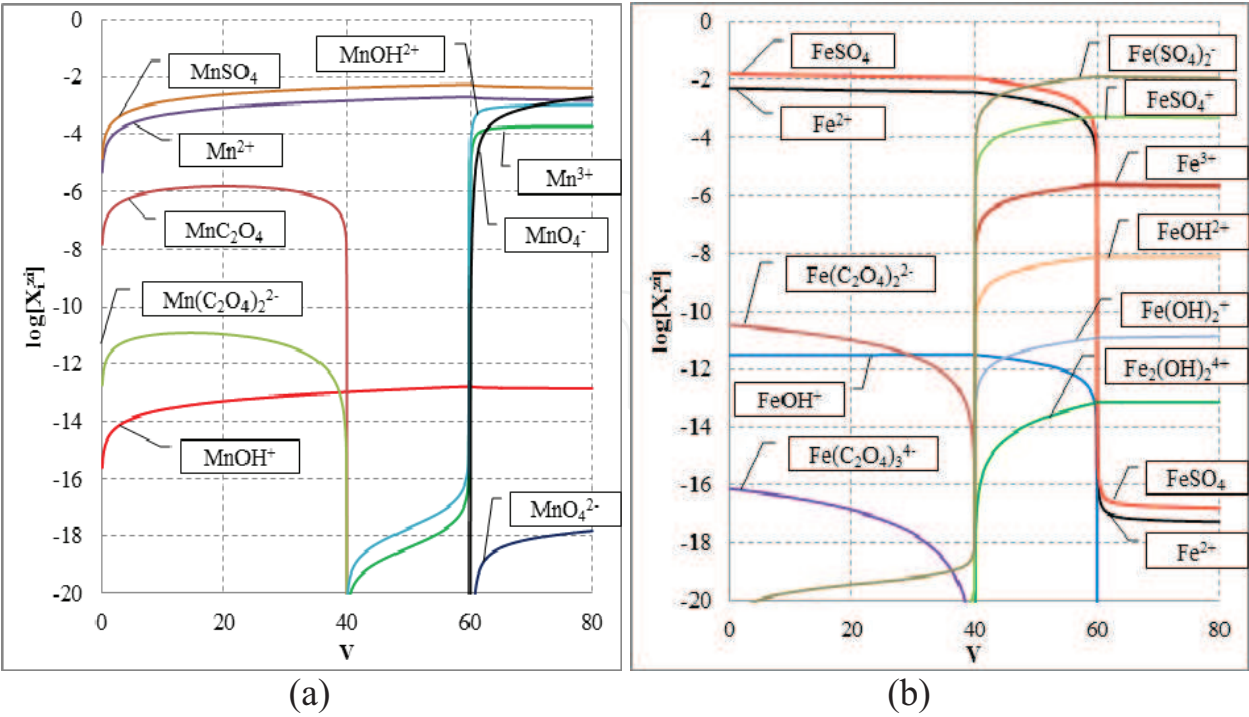
Figure 3. The speciation curves plotted for (a) Mn and (b) Fe species at $V_0 = 100$, $C = 0.02$, $C_{03} = 0.5$, $C_1 = C_{04} = 0.001$ and $C_{01} = C_{02} = 0.002$.
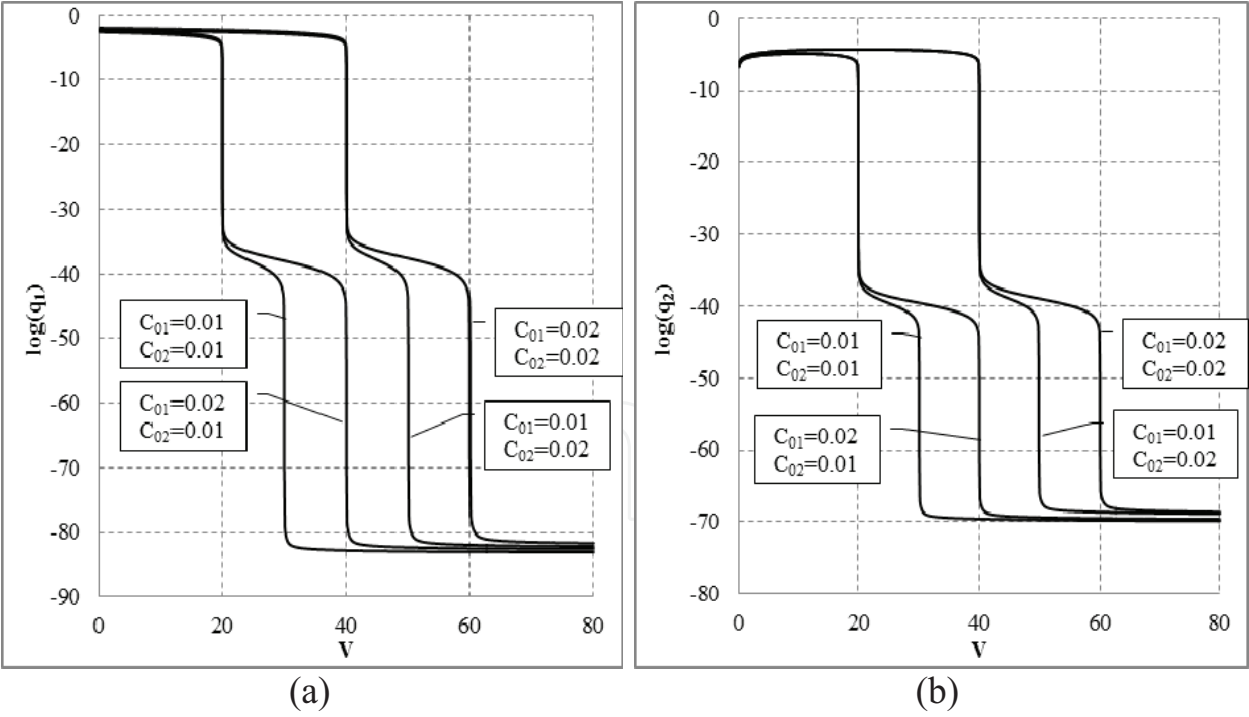

Figure 4. The $\log(q_i)$ versus V relationships (see Eq. (31)) plotted for (a) Fe (i = 1) and (b) Mn (i = 2) oxalates.

There are valid relationships: $CV_{eq1} = 0.2 \cdot C_{01} V_0$ for iron and $CV_{eq2} = 0.4 \cdot C_{02} V_0$ for oxalate. For $V_0 = 100$, $C = 0.02$ we have, in particular, $V_{eq1} = 10$ and $V_{eq2} = 20$ at $C_{01} = 0.01$, $C_{02} = 0.01$ and $V_{eq1} = 20$ and $V_{eq2} = 40$ at $C_{01} = 0.02$ and $C_{02} = 0.02$. This agrees exactly with the position of the points
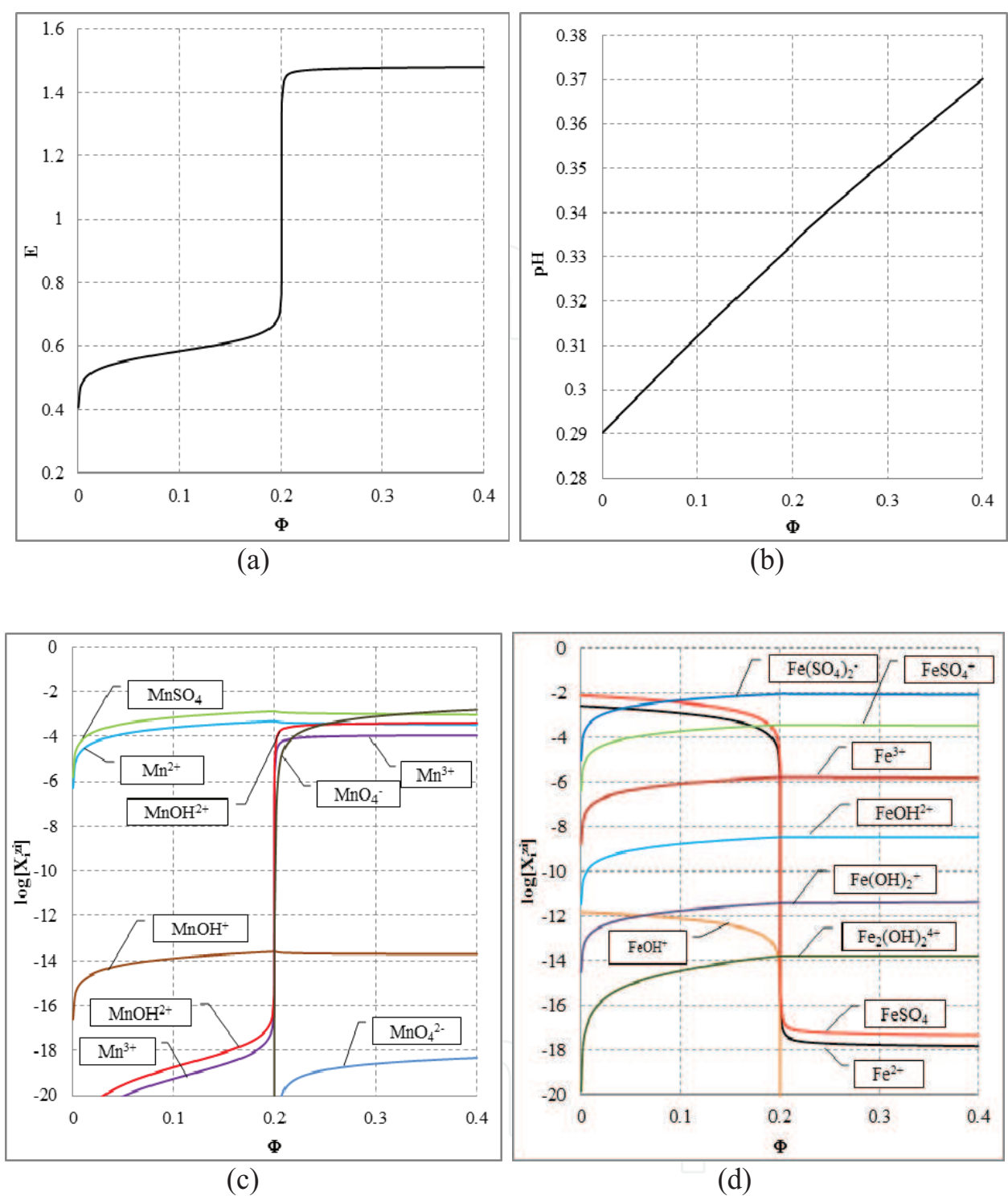
Figure 5. The relationships: (a) $E = E(\Phi)$, (b) $pH = pH(\Phi)$ and the speciation curves $\log[X_i^{z_i}]$ versus Φ for (c) manganese and (d) iron species plotted for titration of $V_0 = 100$ mL of $C_0 = 0.01$ mol/L $FeSO_4 + C_{01}$ mol/L H_2SO_4 as D with V mL of $C = 0.02$ mol/L $KMnO_4$ as T.

where jumps of potential E occur and should be compared with the plots of titration curves for individual analytes: $FeSO_4$ (**Figure 5a**) and $H_2C_2O_4$ (**Figure 6a**), where abscissas are expressed in terms of the fraction titrated Φ (Eq. (5)). The related pH versus Φ relationships are presented in **Figures 5b** and **6b**. To explain/formulate the reactions occurred in the systems together with

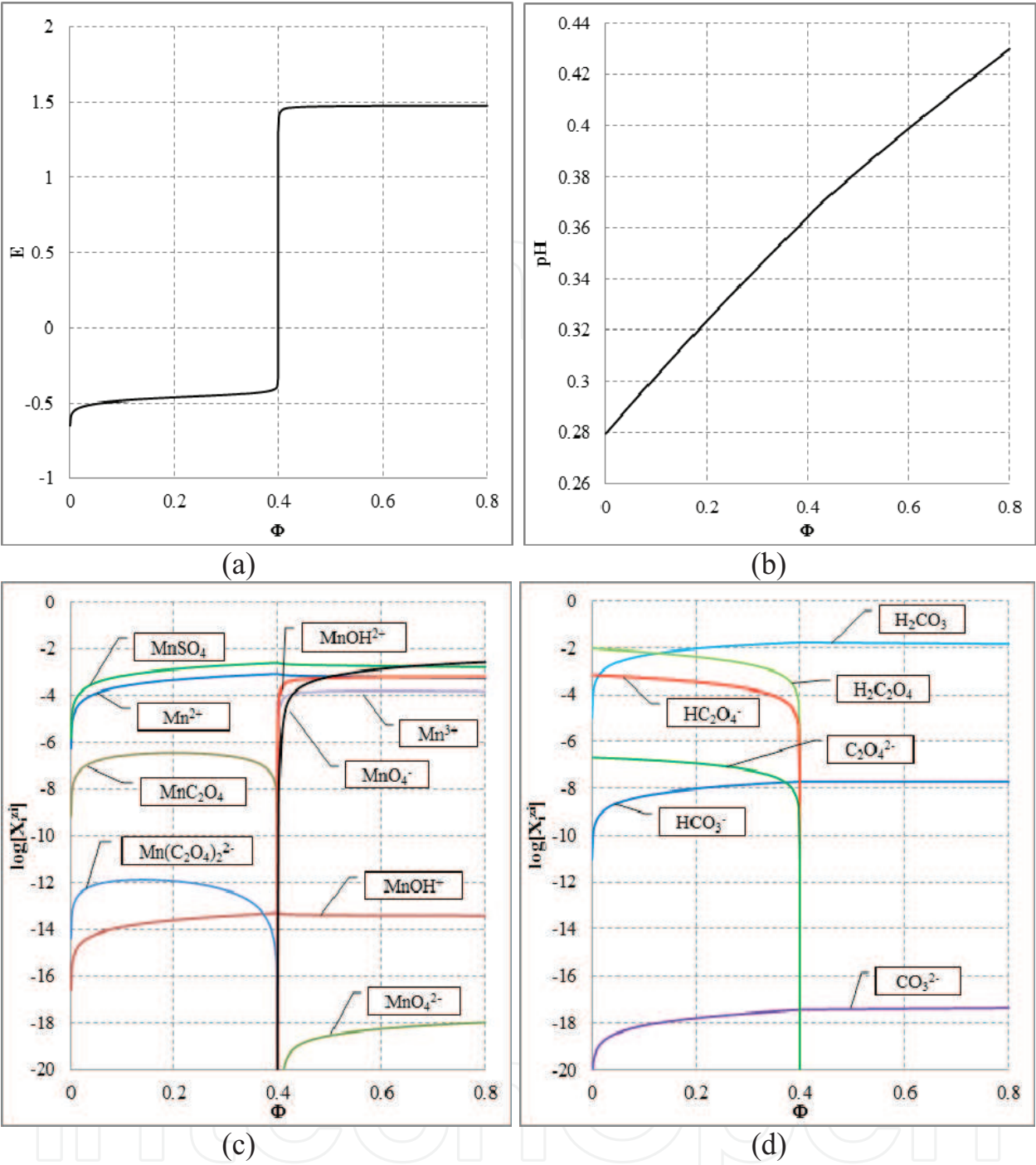**Figure 6.** The relationships: (a) E = E(Φ), (b) pH = pH(Φ) and the speciation curves $\log[X_i^{zi}]$ for (c) Mn-, (d) C-species for titration of $V_0 = 100$ mL of $C_0 = 0.01$ mol/L $H_2C_2O_4 + C_{01}$ mol/L H_2SO_4 as D with V mL of C = 0.02 mol/L $KMnO_4$ as T.

their relative efficiencies, the speciation diagrams depicted in **Figures 3a**, **b**, and **5c**, **d** are used. From **Figure 4a** and **b**, we see that

$$q_1 = [Fe^{+2}][C_2O_4^{-2}]/K_{sp1} < 1 \quad \text{and} \quad q_2 = [Mn^{+2}][C_2O_4^{-2}]/K_{sp2} < 1 \tag{31}$$

i.e., the precipitates **FeC₂O₄** (K_{sp1}) and **MnC₂O₄** (K_{sp2}) do not exist in this system as the equilibrium solid phases at the pre-assumed sufficiently high concentration C_{03} of H_2SO_4; **MnO₂** is not formed there as well, i.e., $a_1 = a_2 = 0$ in Eqs. (26)–(28).

14. Deficiency and veracity of equilibrium data

In some 'variations on the subject', we try to know what would happen if some constraints put on the metastable system are removed and the reaction is conducted in a thermodynamic manner, in accordance with the conditions imposed by the equilibrium constants [1, 36]. One can also analyze the data resulting from (intentional) omission or (factual, presupposed) incomplete physicochemical knowledge on the system studied.

Some computer simulations can be used to check some effects involved with complexation phenomena. For example, we intend to check the effect involved with formation of sulfate complexes $FeSO_4$, $MnSO_4$ and (particularly) $FeSO_4^{+1}$, $Fe(SO_4)_2^{-1}$ in the system (I) $\Rightarrow$ (II). The shapes of the titration curves $E = E(\Phi)$ are compared in **Figure 7**.
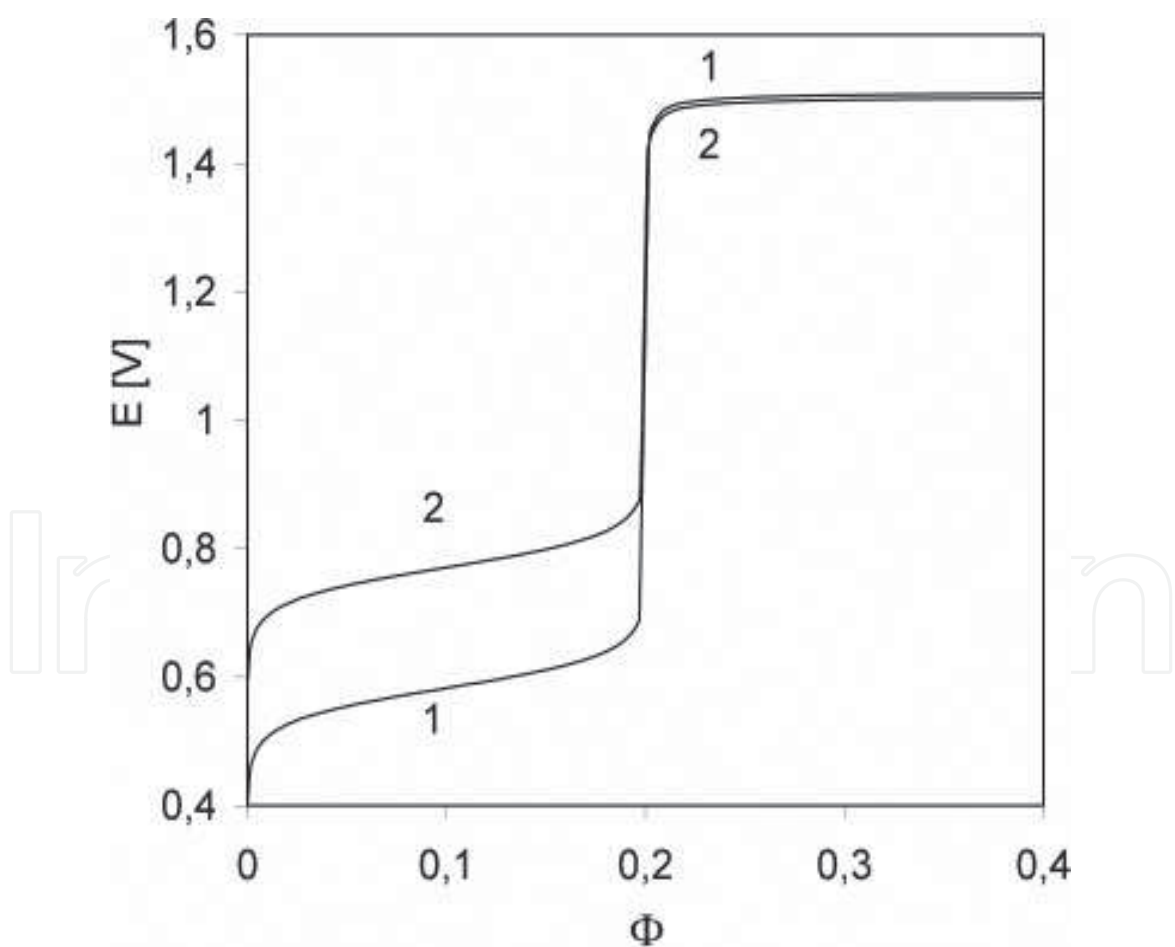

Figure 7. The E versus Φ relationships plotted for the system (I) $\Rightarrow$ (II): (1) at pre-assumed physicochemical knowledge and (2) after intentional omission of all sulfate complexes; $C_0 = 0.01$, $C_{01} = 1.0$ and $C = 0.02$.
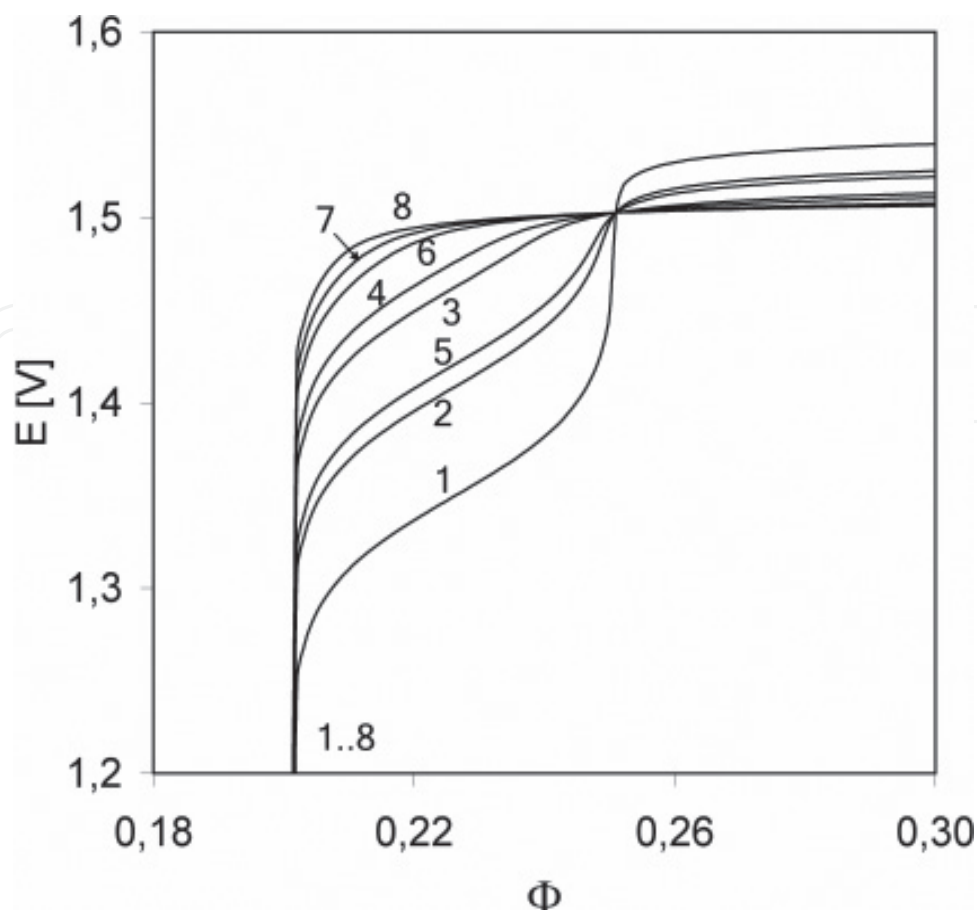
Figure 8. Fragments of hypothetical titration curves for $V_0 = 100$ mL of $FeSO_4$ ($C_0 = 0.01$ mol/L) + H_2SO_4 ($C_{a0} = 0.1$ mol/L) titrated with $C = 0.02$ mol/L $KMnO_4$, plotted at different pairs of stability constants (K_{31}, K_{32}) of the sulfate complexes $Mn(SO_4)_i^{+3-2i}$: (1) (10^4, 10^7), (2) (10^3, 10^6), (3) ($10^{2.5}$, 10^5), (4) (10^2, 10^4), (5) (10^4, 0), (6) (10^3, 0), (7) (10^2, 0) and (8) (0, 0).

Some equilibrium constants used in calculations may be unknown/doubtful on the stage of collection of equilibrium data. In such instances, the pre-assumed/virtual data can be introduced for comparative purposes, and the effects involved with omission/inclusion of some types of complexes can be checked.

The possible a priori complexes of $Mn(SO_4)_i^{+3-2i}$ are unknown in literature. To check the effect of formation of these complexes on the shape of the titration curve $E = E(\Phi)$ in the system (I) $\Rightarrow$ (II), the pre-assumed stability constants K_{3i} of the complexes, $[Mn(SO_4)_i^{+3-2i}] = K_{3i}[Mn^{3+}][SO_4^{2-}]^i$, specified in legend for **Figure 8**, were applied in the related algorithm, where concentrations of $MnSO_4^{+1}$ and $Mn(SO_4)_2^{-1}$ with the corresponding multipliers were inserted in electron (GEB) and charge balances and in concentration balances for Mn and sulfate. As we see, at higher K_{3i} values (comparable to ones related to $Fe(SO_4)_i^{+3-2i}$ (i=1,2) complexes [39]), the new inflection point appears at $\Phi = 0.25$ and disappears at lower K_{3i} values assumed in the simulating procedure. Comparing the simulated curves with the one obtained experimentally [25], one can conclude that the complexes $Mn(SO_4)_i^{+3-2i}$ do not exist at all or the K_{3i} values are small, when compared with those for $Fe(SO_4)_i^{+3-2i}$ [33].

Other interesting examples involved with 'variations on the subject' are presented in Ref. [1], and other references cited therein.

15. Advantages of GATES and usefulness of chemical processes simulation

Mathematical formalism of electrolytic systems tested and resolved according to GATES principles formulated by Michałowski (1992) arises from synthesis of the three laws: (1°) law of charge conservation, (2°) law of elements conservation and (3°) law of mass action. All other chemical laws result from conjunction of those laws; it particularly refers to the stoichiometry and equivalent mass concepts.

GATES, based on physical, physicochemical and chemical laws, is considered as the best thermodynamic approach to equilibrium, non-equilibrium and metastable, mono- and polyphase, static and dynamic, and redox and non-redox systems, of any degree of complexity, with liquid-liquid extraction systems included [31].

GATES related to redox systems is denoted as GATES/GEB. All these systems are resolvable with use of iterative computer programs, for example, MATLAB. The complexity of chemical systems is here of a secondary importance from the point of view of the computational capabilities inherent in iterative computer programs.

GATES is a confirmation of the thesis that 'everything brilliant is simple'. GATES/GEB is the unique tool to obtain information about the thermodynamics of redox systems on the basis of balances and equilibrium constants values.

GATES enables to simulate all possible (from a thermodynamic point of view) processes obtained after pre-assumed crossing of one or more reaction paths in metastable systems.

GATES enables to simulate the processes impossible to track experimentally; for example, dissolving a solid phase in the electrolytic system of a pre-established composition.

GATES relies on the assumption that the chemistry involved with such systems is predictable on the basis of knowledge of physicochemical properties of the species involved in the system in question. A complete set of non-contradictory relations for the equilibrium constants must be used in calculations; this 'iron rule' of mathematics is then obligatory also in calculations related to electrolytic systems.

GATES is the intrinsically consistent theory, joining fundamental laws of physics and chemistry [10, 28]. The knowledge gaining from redox systems is the most comprehensive way for studying such systems. Note that equations-based simulations are most commonly used in physics and related sciences.

GATES joins, on the thermodynamic basis, four kinds of chemical interactions, named as acid-base, redox, precipitation and complexation reactions, extended on a liquid-liquid extraction in

mono- and poly-phase systems. To a certain degree—one can perceive GATES as a spitting image of theory of everything (ToE), as the main, still unresolved issue in physics, aiming to elaborate the consistent theory, that links together four: strong, weak, electromagnetic and gravitational interactions.

GATES referred to electrolytic non-redox and redox systems and is considered as the best thermodynamic approach to such systems. GATES, based on physical (charge conservation), physicochemical (conservation of elements) and chemical (mass action) laws, is the best tool applicable for computer simulation of equilibrium, non-equilibrium and metastable, and mono- and poly-phase electrolytic systems. GATES is the basis for the Generalized Equiva-lence Mass (GEM) concept, with no relevance to the chemical reaction notation.

One can also express a conviction that the discovery of the Approach II to GEB in context with GATES will lead to gradual elimination of the stoichiometry concept from the consciousness of chemists.

16. Final comments

This chapter provides comprehensive, compatible and consistent knowledge on modeling electrolytic redox and non-redox systems and further steps applied to gain the thermodynamic knowledge on the systems, referred mainly to aqueous media.

The Generalized Electron Balance (GEB) concept, related to electrolytic redox systems, is put in context with the principle of conservation of all elements in electrolytic redox systems, in aqueous, non-aqueous or mixed-solvent media. The GEB is fully compatible with charge and concentration balances, and completes the set of 2 + k equations needed for quantitative description of a redox system, with 2 + k independent/scalar variables $\mathbf{x}^T = (E, pH, pX_1,\ldots, pX_k)$. Two equivalent approaches (I and II) to GEB were proposed (1992, 2006) by Michałowski. The Approach I to GEB is based on a card-game principle, with electron-active elements as gamblers, electron-non-active elements as fans and common pool of electrons introduced by electron-active elements as money. The Approach II to GEB is based on the linear combination $2f(O)-f(H)$ of elemental balances: $f(H)$ for H and $f(O)$ for O. The linear independency/dependency of $2f(O)-f(H)$ from charge and other elemental/core balances referred to the system in question provides the general criterion distinguishing between redox and non-redox systems. For non-redox systems, $2f(O)-f(H)$ is the linear combination of those balances, that is, it is not a new, independent equation in such systems. In redox systems, $2f(O)-f(H)$ is the independent equation, considered as the primary form of GEB and denoted as pr-GEB. The balances for elements/cores $\neq$ H, O are the basis for k concentration balances, forming—with GEB and charge balance—the set of 2+k independent balances, expressed in terms of concentrations. The Approach I to GEB, considered as the 'short' version of GEB, can be applied if the oxidation numbers for all elements in components forming a system and in the species of the system are known beforehand. The Approach II to GEB needs none prior information on oxidation numbers of all elements in the components and species in the system.

Within the Approaches I and II to GEB, the roles of oxidants and reducers are not ascribed to the components and particular species. The GEB is put in context with the Generalized Approach to Electrolytic Systems (GATES) as GATES/GEB, where all quantitative thermodynamic knowledge on the redox system is involved in the complete set of independent equilibrium constants, where standard potentials E_{0i} are involved. The GATES/GEB provides the best thermodynamic formulation of electrolytic redox systems of any degree of complexity, namely: equilibrium, non-equilibrium and metastable, mono- and poly-phase and static and dynamic electrolytic systems, resolvable with the use of iterative computer programs, applied to the set of nonlinear equations, with no simplifying assumptions needed. The GATES/GEB can also be referred to as redox systems in mixed-solvent media, provided that the related thermodynamic knowledge is attainable. This chapter is referred to dynamic systems, realized according to the titrimetric mode. The results obtained from the calculations can be presented graphically on 2*D* or 3*D* diagrams. The speciation diagrams obtained according to GATES/GEB have indisputable advantage over Pourbaix predominance diagrams. The GEB concept, unknown before 1992, is perceived as an emanation of the matter/elements conservation, as the general law of nature. The redox systems are formulated on simple principles, unknown in earlier literature. Earlier approaches to electrolytic redox systems, based on stoichiometric principles, are thus invalidated.

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