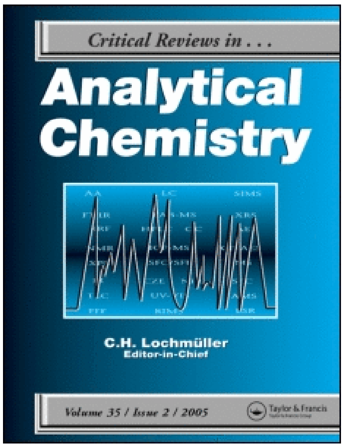

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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Tadeusz Michałowski[a]
[a] Faculty of Chemical Engineering and Technology, Cracow University of Technology, Cracow, Poland

To cite this Article Michałowski, Tadeusz(2010) 'The Generalized Approach to Electrolytic Systems: I. Physicochemical and Analytical Implications', Critical Reviews in Analytical Chemistry, 40: 1, 2 — 16
To link to this Article: DOI: 10.1080/10408340903001292
URL: http://dx.doi.org/10.1080/10408340903001292

Critical Reviews in Analytical Chemistry, 40:2–16, 2010

ISSN: 1040-8347 print / 1547-6510 online
DOI: 10.1080/10408340903001292

The Generalized Approach to Electrolytic Systems: I. Physicochemical and Analytical Implications

Tadeusz Michałowski
Faculty of Chemical Engineering and Technology, Cracow University of Technology, Cracow, Poland

The generalized electron balance (GEB) concept is derived from elementary rules of the matter preservation and applied for resolution of complex electrolytic systems, with special emphasis put on redox systems. Interrelations between different fundamental rules of the matter preservation, referred to electrolytic systems, are indicated. Equilibrium and metastable systems are considered. Advantages of the generalized approach to electrolytic systems (GATES) are evidenced.

Keywords equilibrium analysis, titration, computer simulation

INTRODUCTION

Dynamic processes in electrolytic systems, e.g. titrations, are involved with acid–base, redox, complexation, and precipitation reactions. However, except simple acid–base titrations, it is difficult to indicate a system where only one type of the reaction occurs. As a rule, the systems considered in analytical practice involve different types of reactions and, moreover, a particular type of the reaction, e.g., complexation, is exemplified by different representatives, e.g., different ligands.

Concentrations of the species in any electrolytic system are interrelated in different constraints: material balances and expressions for equilibrium constants. Both kinds of interrelations, of algebraic nature, are the basis for thermodynamic description of such systems. In this paper, a special emphasis is put on dynamic redox systems.

The importance of redox systems in analytical chemistry is unquestionable. In this respect, a slight number of papers related to redox systems issued hitherto testifies unambiguously that the generalized electron balance (GEB) concept, devised by Michałowski (1992) (1, 2) and proved as the missing link bracing the quantitative description of redox systems, is still unknown or incomprehensible to chemists, and analysts in particular. One of the main purposes of the present paper is to provide a new approach to the GEB concept and familiarize it to a wider community.

The current paper aims also to indicate the close relationships between different rules of conservation, and to provide some examples indicating huge possibilities inherent in the generalized approach to electrolytic systems (GATES) (see (3–6) and references cited therein). This way, one can simulate (imitate) any analytical prescription referred to any process that may be realized under isothermal conditions, exemplified by pH-static titrations (7, 8). The GATES refers to mono– and two-phase systems (9–13), with liquid–liquid extraction systems included (10).

Considering any electrolytic system from the matter conservation viewpoint, one should refer to a closed system containing condensed phase(s) and separated from its surroundings by diathermal walls. In a closed system, no matter exchange between the system and its surroundings occurs. Diathermal walls allow the heat exchange that is the prerequisite to follow the process under isothermal conditions in the systems, where exo- or endothermic reactions take place.

Electrolytic systems can be considered from thermodynamic or kinetic viewpoints. The thermodynamic approach can be applied to equilibrium or metastable systems (Fig.1). In equilibrium systems, all reaction paths are accessible whereas in metastable systems at least one of the reaction paths among ones attainable from an equilibrium viewpoint is inaccessible, under defined conditions of the procedure applied for this purpose. In other words, not all reactions, possible from the thermodynamic viewpoint, occur under defined conditions assumed. The activation barriers for some reaction paths are not crossed, i.e., the resulting reactions cannot proceed in a metastable system. For example, permanganate is in a metastable state with water and then the reaction

$$4MnO_4^- + 2H_2O = 4MnO_2 + 3O_2 + 4OH^-$$

foreseen from the thermodynamic viewpoint, does not occur, even at elevated temperatures.

Address correspondence to Tadeusz Michałowski, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland. E-mail: michalot@o2.pl

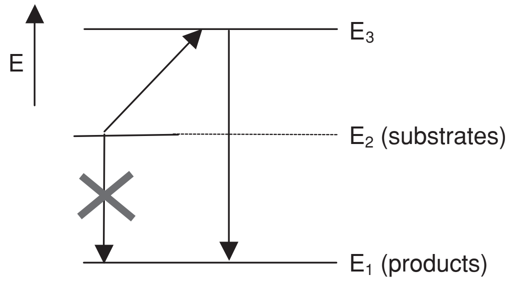

FIG. 1. Explanation of metastable state (energy E_2) for substrates. The immediate spontaneous transition to the level E_1 is forbidden. $E_3 - E_2$ is the activation energy needed for transition of the substrates into products.

In order to confirm the metastable state in simulated calculations, one should omit all possible products forbidden by a reaction barrier on the related route, from the related balances. On the other hand, one can make free some reaction routes and check "what would happen." For example, the effect of (possible *a priori*) the formation of complexes $Mn(SO_4)_i^{+3-2i}$ on the shape of the potentiometric titration curve $E = E(\Phi)$ in Fe(II) – MnO_4^- system has been considered in ref. (11).

The current paper will also concern the interrelations between equilibrium and metastable systems. It will be indicated that the simulated thermodynamic analysis enables one to follow different pathways and determine the corresponding relationships with measurable quantities involved, such as pH or voltage E of the electrolytic cell versus volume V of titrant added. Comparison of the simulated curves with ones obtained experimentally enables one to explain the reactions that occurred in the system, on any stage of the process tested. The speciation analysis made for this purpose enables one to formulate the accompanying reactions, together with their efficiencies.

It will also be clearly indicated that a non-redox system is a particular case of a redox system. It provides a kind of uniformity in the formulae derived for this purpose. Non-redox and redox systems will be exemplified later.

RULES OF CONSERVATION—EXAMPLES

The conservation rules can be related to elements, orbital electrons, and protons (those in nuclei) and referred to as closed systems, separated from the environment by diathermal walls. We further confine our discussion to the systems where no nuclear transformations occur. The neutrons will be omitted in quantitative description, for simplicity; it enabled us to omit the isotopic effects and abundances of different nuclides. In such systems, the neutrons are bounded with protons within the corresponding nuclei. It should be noticed that the external charge of a species originates from the numbers of protons in nuclei and orbital electrons in atoms forming these species.

Some rules of conservation are interdependent and this fact will be raised in examples of simple and more complex electrolytic systems. This interdependency and indication of the set of independent relations will be considered in examples where formation of aqua–complexes by ionic and neutral species will also be taken into account.

In some examples considered below, the system (solution) of volume V [mL] will be formed by mixing N molecules of a substance (solute) X with N_w molecules of water. The number of the species (entities) X_i in the system will be denoted by N_i. Molar concentration of solute X will be denoted by

$$C = N/(10^{-3} \cdot N_A V) \qquad [1]$$

and molar concentration of the species X_i by

$$[X_i] = N_i/(10^{-3} \cdot N_A V) \qquad [2]$$

where N_A is Avogadro's number. In the balances written in terms of concentrations, hydrating water particles will be omitted, for simplicity. The additivity in volumes of solutions will be assumed, i.e., the volume of the mixture D+T formed of V_0 mL of titrand (D) and V mL of titrant (T) will be equal V_0+V mL.

Example 1 (Non–Redox System)

Let us consider the system composed of N particles of C_6H_5COOH and N_w particles of H_2O. In the mathematical description of the solution (V mL) thus formed, the formation of hydrated species (ions, particles) is admitted. Then we have:

N_1 particles of H_2O, N_2 ions $H^+ \cdot n_2H_2O$, N_3 ions $OH^- \cdot n_3H_2O$, N_4 particles of $C_6H_5COOH \cdot n_4H_2O$, and N_5 ions $C_6H_5COO^- \cdot n_5H_2O$; $n_2, \ldots, n_5$ denote the mean number of H_2O molecules associated to the corresponding entities: H^+, OH^-, C_6H_5COOH, and $C_6H_5COO^-$; $n_i \geq 0$. Atomic numbers: $Z_1 = 1$ for H, $Z_2 = 8$ for O, $Z_3 = 6$ for C. On this basis, one can formulate the following balances:

- for C : $7N_4 + 7N_5 = 7N$, i.e., $N_4 + N_5 = N$ [3]
- for H : $2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + N_4(6 + 2n_4) + N_5(5 + 2n_5) = 6N + 2N_w$ [4]
- for O : $N_1 + N_2n_2 + N_3(1 + n_3) + N_4(2 + n_4) + N_5(2 + n_5) = 2_N + N_w$ [5]
- for protons : $N_1(2Z_1 + Z_2) + N_2(Z_1 + n_2(2Z_1 + Z_2)) + N_3(Z_1 + Z_2 + n_3(2Z_1 + Z_2)) + N_4(6Z_1 + 2Z_2 + 7Z_3 + n_4(2Z_1 + Z_2)) + N_5(5Z_1 + 2Z_2 + 7Z_3 + n_5(2Z_1 + Z_2)) = N(6Z_1 + 2Z_2 + 7Z_3) + N_w(2Z_1 + Z_2)$ [6]
- for electrons : $N_1(2Z_1 + Z_2) + N_2(Z_1 - 1 + n_2(2Z_1 + Z_2)) + N_3(Z_1 + Z_2 + 1 + n_3(2Z_1 + Z_2)) + N_4(6Z_1 + 2Z_2 + 7Z_3 + n_4(2Z_1 + Z_2)) + N_5(5Z_1 + 2Z_2 + 7Z_3 + 1 + n_5(2Z_1 + Z_2)) = N(6Z_1 + 2Z_2 + 7Z_3) + N_w(2Z_1 + Z_2)$ [7]

From the combination of Eqs. [4] and [5] we have

$$N_2 - N_3 + 2N_4 + N_5 = 2N \qquad [8]$$

whereas from [6] and [7]

$$N_2 = N_3 + N_5 \qquad [9]$$

Note that [8] is the linear combination of Eqs. [3] and [9], obtained after multiplying [3] by 2 and adding the sides to Eq. [9]. Applying the formulae [1] and [2], from [3] and [9] we get the concentration balance for benzoic acid

$$[C_6H_5COOH] + [C_6H_5COO^-] = C \qquad [3a]$$

and charge balance

$$[H^+] - [OH^-] - [C_6H_5COO^-] = 0 \qquad [9a]$$

respectively. The balance $[H^+] - [OH^-] + 2[C_6H_5COOH] + [C_6H_5COO^-] = 2C$ was obtained from [8], [1] and [2] is then a linear combination of charge and concentration balances, i.e., the balances for H and O do not provide the balance (linearly) independent on [3a] and [9a]. In other words, the charge balance [9a] together with the concentration balance [3a] form the complete set of independent balances related to this (non-redox) system.

Example 2 (Non–Redox System)

For the system composed of N particles of $CuSO_4 \cdot 5H_2O$ and N_w particles of H_2O (4), where the following species:

H_2O (N_1), $H^+ \cdot n_2H_2O$ (N_2), $OH^- \cdot n_3H_2O$ (N_3), $Cu^{2+} \cdot n_4H_2O$ (N_4), $CuOH^+ \cdot n_5H_2O$ (N_5), soluble complex $Cu(OH)_2 \cdot n_6H_2O$ (N_6), $Cu(OH)_3^- \cdot n_7H_2O$ (N_7), $Cu(OH)_4^{2-} \cdot n_8H_2O$ (N_8), complex $CuSO_4 \cdot n_9H_2O$ (N_9), $HSO_4^- \cdot n_{10}H_2O$ (N_{10}), and $SO_4^{2-} \cdot n_{11}H_2O$ (N_{11})
are formed, $n_i \geq 0$, one can write the balances:

- for Cu : $N_4 + N_5 + N_6 + N_7 + N_8 + N_9 = N \qquad [10]$
- for S : $N_9 + N_{10} + N_{11} = N \qquad [11]$
- for H : $$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + 2N_4n_4 + N_5(1 + 2n_5) + N_6(2 + 2n_6) + N_7(3 + 2n_7) + N_8(4 + 2n_8) + 2N_9n_9 + N_{10}(1 + 2n_{10}) + 2N_{11}n_{11} = 10N + 2N_w \qquad [12]$$
- for O : $$N_1 + N_2n_2 + N_3(1 + n_3) + N_4n_4 + N_5(1 + n_5) + N_6(2 + n_6) + N_7(3 + n_7) + N_8(4 + n_8) + N_9(4 + n_9) + N_{10}(4 + n_{10}) + N_{11}(4 + n_{11}) = 9N + N_w \qquad [13]$$
- for protons : $$N_1(2Z_1 + Z_2) + N_2(Z_1 + n_2(2Z_1 + Z_2)) + N_3(Z_2 + Z_1 + n_3(2Z_1 + Z_2)) + N_4(Z_3 + n_4(2Z_1 + Z_2)) + N_5(Z_3 + Z_2 + Z_1 + n_5(2Z_1 + Z_2)) + N_6(Z_3 + 2(Z_2 + Z_1) + n_6(2Z_1 + Z_2)) + N_7(Z_3 + 3(Z_2 + Z_1) + n_7(2Z_1 + Z_2)) + N_8(Z_3 + 4(Z_2 + Z_1) + n_8(2Z_1 + Z_2)) + N_9(Z_3 + Z_4 + 4Z_2 + n_9(2Z_1 + Z_2)) + N_{10}(Z_1 + Z_4 + 4Z_2 + n_{10}(2Z_1 + Z_2)) + N_{11}(Z_4 + 4Z_2 + n_{11}(2Z_1 + Z_2)) = N(Z_3 + Z_4 + 4Z_2 + 5(2Z_1 + Z_2)) + N_w(2Z_1 + Z_2) \qquad [14]$$
- for electrons : $$N_1(2Z_1 + Z_2) + Z_2(Z_1 - 1) + n_2(2Z_1 + Z_2)) + N_3(Z_2 + Z_1 + 1 + n_3(2Z_1 + Z_2)) + N_4(Z_3 - 2 + n_4(2Z_1 + Z_2)) + N_5(Z_3 + Z_2 + Z_1 - 1 + n_5(2Z_1 + Z_2)) + N_6(Z_3 + 2(Z_2 + Z_1) + n_6(2Z_1 + Z_2)) + N_7(Z_3 + 3(Z_2 + Z_1) + 1 + n_7(2Z_1 + Z_2)) + N_8(Z_3 + 4(Z_2 + Z_1) + 2 + n_8(2Z_1 + Z_2)) + N_9(Z_3 + Z_4 + 4Z_2 + n_9(2Z_1 + Z_2)) + N_{10}(Z_1 + Z_4 + 4Z_2 + 1 + n_{10}(2Z_1 + Z_2)) + N_{11}(Z_4 + 4Z_2 + 2 + n_{11}(2Z_1 + Z_2)) = N(Z_3 + Z_4 + 4Z_2 + 5(2Z_1 + Z_2)) + N_w(2Z_1 + Z_2) \qquad [15]$$

where the atomic numbers are: $Z_1 = 1$ for H, $Z_2 = 8$ for O, $Z_3 = 29$ for Cu, and $Z_4 = 16$ for S.

From [12] and [13] we get the relation

$$-N_2 + N_3 + N_5 + 2N_6 + 3N_7 + 4N_8 + 8N_9 + 7N_{10} + 8N_{11} = 8N \qquad [16]$$

whereas from [14] and [15] one obtains the starting form of charge balance

$$N_2 - N_3 + 2N_4 + N_5 - N_7 - 2N_8 - N_{10} - 2N_{11} = 0 \qquad [17]$$

Note 1. In general, the charge balance is derivable from balances for electrons and protons, i.e., it is the linear combination of balances for protons and electrons. It is nothing strange because the external charge of a species is a simple sum of charges brought by protons and electrons. In further examples, the balances for protons and electrons will then be omitted, both for redox and non-redox systems (4) and the charge balance will be introduced immediately. Moreover, it should be noticed that population of water molecules does not enter this equation obtained from balances for H and O. These regularities occur, after all, for any non-redox or redox system.

Multiplication of [10] by 2, [11] by 6, and [17] by –1 and addition by sides, gives the Eq. [16]; Eq. [16] is then the linear combination of Eqs. [10], [11], and [17]. Applying the formulae [1] and [2], we get the concentration balances for Cu, S and the charge balance:

$$[Cu^{2+}] + \sum_{i=1}^{4} \left[Cu(OH)_i^{+2-i}\right] + [CuSO_4] - C = 0 \qquad [18]$$

$$[HSO_4^-] + \left[SO_4^{2-}\right] + [CuSO_4] - C = 0 \qquad [19]$$

$$[H^+] - [OH^-] + 2\left[Cu^{2+}\right] + \sum_{i=1}^{4} (2 - i)\left[Cu(OH)_i^{+2-i}\right] - [HSO_4^-] - 2\left[SO_4^{2-}\right] = 0 \qquad [20]$$

as the set of linearly independent equations.

Example 3 (Redox System)

Let the system be composed of N molecules KBrO and N_w molecules of H_2O. In volume V [mL] of the system thus obtained, there are the following species: $HBrO_3$ (N_1, n_1), BrO_3^- (N_2, n_2), HBrO (N_3, n_3), BrO^- (N_4, n_4), Br_2 (N_5, n_5), Br_3^- (N_6, n_6), Br^-(N_7, n_7), H^+ (N_8, n_8), OH^- (N_9, n_9), Na^+ (N_{10}, n_{10}), and H_2O (N_{11}). The notation X_i (N_i, n_i) indicate the number N_i of individual entities and mean number n_i of water molecules attached to X_i. Denoting atomic numbers for H, O, Br, and K by $Z_H = 1$, $Z_O = 8$, $Z_{Br} = 35$, and $Z_K = 19$, respectively, we write the balances:

- for H:

$$\begin{aligned} &N_1 \cdot (1 + 2n_1) + N_2 \cdot 2n_2 + N_3 \cdot (1 + 2n_3) + N_4 \cdot 2n_4 \\ &\quad + N_5 \cdot 2n_5 + N_6 \cdot 2n_6 + N_7 \cdot 2n_7 + N_8 \cdot (1 + 2n_8) \\ &\quad + N_9 \cdot (1 + 2n_9) + 2N_{10} = 2N_w \qquad [21] \end{aligned}$$

- for O:

$$\begin{aligned} &N_1 \cdot (3 + n_1) + N_2 \cdot (3 + n_2) + N_3 \cdot (1 + n_3) \\ &\quad + N_4 \cdot (1 + n_4) + N_5 \cdot n_5 + N_6 \cdot n_6 + N_7 \cdot n_7 \\ &\quad + N_8 \cdot n_8 + N_9 \cdot (1 + n_9) + N_{10} = N + N_w \qquad [22] \end{aligned}$$

- for Br:

$$N_1 + N_2 + N_3 + N_4 + 2N_5 + 3N_6 + N_7 = N \qquad [23]$$

$$\begin{aligned} &[HBrO_3] + [BrO_3^-] + [HBrO] + [BrO^-] \\ &\quad + 2[Br_2] + [Br^-] = C \qquad [23a] \end{aligned}$$

- for K:

$$N_{10} = N \qquad [24]$$

$$[K^+] = C \qquad [24a]$$

From [21] and [22]:

$$5N_1 + 6N_2 + N_3 + 2N_4 - N_8 + N_9 = 2N \qquad [25]$$

$$\begin{aligned} &5[HBrO_3] + 6[BrO_3^-] + [HBrO] + 2[BrO^-] \\ &\quad - [H^+] + [OH^-] = 2C \qquad [25a] \end{aligned}$$

The charge balance is as follows:

$$-N_2 - N_4 - N_6 - N_7 + N_8 - N_9 + N_{10} = 0 \qquad [26]$$

$$\begin{aligned} &-[BrO_3^-] - [BrO^-] - [Br_3^-] - [Br^-] + [H^+] \\ &\quad - [OH^-] + [K^+] = 0 \qquad [26a] \end{aligned}$$

From [24]–[26] we get

$$5(N_1 + N_2) + N_3 + N_4 - N_6 - N_7 = N \qquad [27]$$

Subtracting [27] from [23] multiplied by Z_{Br} and applying [1] and [2] we get, by turns,

$$\begin{aligned} &(Z_{Br} - 5) \cdot (N_1 + N_2) + (Z_{Br} - 1) \cdot (N_3 + N_4) + 2Z_{Br} \cdot N_5 \\ &\quad + (3Z_{Br} + 1) \cdot N_6 + (Z_{Br} + 1) \cdot N_7 = (Z_{Br} - 1) \cdot N \qquad [28] \end{aligned}$$

$$\begin{aligned} &(Z_{Br} - 5) \cdot ([HBrO_3] + [BrO_3^-]) + (Z_{Br} - 1) \cdot ([HBrO] \\ &\quad + [BrO^-]) + 2Z_{Br} \cdot [Br_2] + (3Z_{Br} + 1) \cdot [Br_3^-] \\ &\quad + (Z_{Br} + 1) \cdot [Br^-] = (Z_{Br} - 1) \cdot C \qquad [28a] \end{aligned}$$

Note that (a) no reaction notations and (b) no calculation of oxidation degrees were needed in this approach to the generalized electron balance concept.

A simpler deduction of Eq. [28a], similar to one presented in (3, 9), can also be applied. For this purpose, it is assumed that all bromine electrons in potassium hypobromite (KBrO) introduced into water were partitioned between particular bromine species, formed in effect of disproportionation; the bromine electrons were balanced. Water particles do not participate in the system as oxidizing or reducing agents. Denoting the atomic number for bromine by Z_{Br} and applying the enumeration presented above, it was assumed that one entity $HBrO_3 \cdot n_4H_2O$ involves Z_{Br}–5 bromine electrons, . . . , one entity $Br_3^- \cdot n_9H_2O$ involves $3Z_{Br}+1$ bromine electrons, and one entity $Br^- \cdot n_{10}H_2O$ involves $Z_{Br}+1$ bromine electrons. On this basis, Eq. [28] and the resulting electron balance (Eq. [28a]) is obtained.

For practical needs, it is far more comfortable (understandable) to apply Eq. [28a], not Eq. [25a], although both equations can be treated equivalently. Simply, Eq. [28a] expresses a kind of "dissipation" process, referred to bromine electrons. Eq. [25a] looks rather strangely in this respect—it is not easy to explain immediately its shape. The idea assumed in Eq. [28a] is very helpful, particularly in the case of more complex redox systems. For example, the electron balance for the system $HBrO_3$ (C_1)+ Br_2 (C_2)+ KBrO (C_3)+ KBr (C_4) has the form

$$\begin{aligned} &(Z_{Br} - 5) \cdot ([HBrO_3] + [BrO_3^-]) + (Z_{Br} - 1) \cdot ([HBrO] \\ &\quad + [BrO^-]) + 2Z_{Br} \cdot [Br_2] + (3Z_{Br} + 1) \cdot [Br_3^-] \\ &\quad + (Z_{Br} + 1) \cdot [Br^-] = (Z_{Br} - 5) \cdot C_1 + 2Z_{Br} \cdot C_2 \\ &\quad + (Z_{Br} - 1) \cdot C_3 + (Z_{Br} + 1) \cdot C_4 \qquad [28b] \end{aligned}$$

Note that the left side of Eq. [28b] is identical with the left side of Eq. [28a], whereas the right side involves the quota of other bromine substances composing the system. Moreover, if the system involves some other substances that (a) do not participate the electron transitions or (b) do not form complexes with bromine species, then the electron balance remains unchanged.

For the mixture formed of V_0 mL of $HBrO_3$ (C_0) and V mL of HBr (C), we get the electron balance (GEB)

$$\begin{aligned} &(Z_{Br} - 5) \cdot ([HBrO_3] + [BrO_3^-]) + (Z_{Br} - 1) \cdot ([HBrO] \\ &\quad + [BrO^-]) + 2Z_{Br} \cdot [Br_2] + (3Z_{Br} + 1) \cdot [Br_3^-] \\ &\quad + (Z_{Br} + 1) \cdot [Br^-] = ((Z_{Br} - 5) \cdot C_0V_0 \\ &\quad + (Z_{Br} + 1) \cdot CV)/(V_0 + V) \qquad [28c] \end{aligned}$$

Note 2. It should necessarily be stressed that the balance for electrons is different from the electron balance, named in (9, 10) as the electron prebalance. Also the balance for protons is different from the proton balance, known as the linear combination of charge and concentration balances, applicable to the systems involving salts (14, 15).

Note 3. The electron balance, exemplified by Eqs. [28a–c], is named as generalized electron balances (GEB). The equations involving the numbers N_i of the species X_i, e.g., Eq. [28], will be named as the rough or starting form of GEB. The idea assumed in the above formulation of GEB is very applicable when some simulating procedures involved with metastable systems are considered.

Note 4. Dissipation of elemental electrons resembles a card-game, owing to the following analogues: active element ↔ gambler, electrons ↔ money, non-active element ↔ fan.

Example 4 (Redox System)

Generalizing the approach presented in Example 3, we assume the species of $H_pO_qX_r^{+z}{\cdot}n_{pqrz}H_2O$ type formed in the system; z is the charge of this species; $z = 0$ (for uncharged species) or $z > 0$ (for cations) or $z < 0$ (for anions); (p,q,r,z) characterizes the species $H_pO_qX_r^{+z}$ different from (2,1,0,0) for H_2O, (1,0,0,1) for H^+, and (1,1,0,–1) for OH^-. Atomic numbers: $Z_1 = 1$ for H, $Z_2 = 8$ for O, and Z_X for X.

Assuming that N molecules $H_PO_QX_R{\cdot}nH_2O$ and N_w molecules of H_2O were mixed together and the solution of volume V [mL] containing N_{pqrz} units of $H_pO_qX_r^{+z}$ type has been thus obtained, we get the elemental balances
for X

$$\sum\nolimits_{pqrz} r \cdot N_{pqrz} = N \cdot R \qquad [29]$$

for H

$$2N_{2100} + N_{1001} \cdot (1 + 2n_{1001}) + N_{110\underline{1}} \cdot (1 + 2n_{110\underline{1}}) + \sum\nolimits_{pqrz} N_{pqrz} \cdot (p + 2 \cdot n_{pqrz}) = N \cdot (P + 2n) + 2N_w \qquad [30]$$

for O

$$N_{2100} + N_{1001} \cdot n_{1001} + N_{110\underline{1}} \cdot (1 + n_{110\underline{1}}) + \sum\nolimits_{pqrz} N_{pqrz} \cdot (q + n_{pqrz}) = N(Q + n) + N_w \qquad [31]$$

Subtracting [30] from [31] multiplied by 2, one gets, successively,

$$N_{100\underline{1}} - N_{110\underline{1}} + \sum\nolimits_{pqrz} (p - 2q) \cdot N_{pqrz} = N \cdot (P - 2Q) \qquad [32]$$

$$[H^+] - [OH^-] + \sum\nolimits_{pqrz} (p - 2q) \cdot \left[H_pO_qX_r^{+z}\right] = (P - 2Q) \cdot C \qquad [32a]$$

The charge balance has the form

$$N_{1001} - N_{110\underline{1}} + \sum\nolimits_{pqrz} z \cdot N_{pqrz} = 0 \qquad [33]$$

$$[H^+] - [OH^-] + \sum\nolimits_{pqrz} z \cdot \left[H_pO_qX_r^{+z} \cdot n_{pqrz}H_2O\right] = 0 \qquad [33a]$$

From comparison of [32a] and [33a], after applying Eqs. [1] and [2], one obtains

$$\sum\nolimits_{pqrz} (2q - p + z) \cdot \left[H_pO_qX_r^{+z} \cdot n_{pqrz}H_2O\right] = (2Q - P) \cdot C \qquad [34]$$

$$\sum\nolimits_{pqrz} Z_X \cdot r \cdot \left[H_pO_qX_r^{+z} \cdot n_{pqrz}H_2O\right] = Z_X \cdot R \cdot C \qquad [35]$$

and then the equation written in terms of the electron (pre)balance (4, 9, 10)

$$\sum\nolimits_{pqrz} (r \cdot Z_X + p - 2 \cdot q - z) \cdot [H_pO_qX_r^{+z} \cdot n_{pqrz}H_2O] = (R \cdot Z_X + P - 2 \cdot Q) \cdot C \qquad [36]$$

is obtained.

Equation [36] is applicable to the systems where disproportionating reactions occur and the species such as $HBrO_3$ and $H_3IO_6^{2-}$ are involved (4). The coefficients (factors) at the concentrations, entering the related electron balances, i.e., $r{\cdot}Z_X + p–2{\cdot}q - z$, are as follows: $1{\cdot}Z_X + 1 - 2{\cdot}3 - 0 = Z_X - 5$ for $HBrO_3$, $1{\cdot}Z_X + 3 - 2{\cdot}6 - (–2) = Z_X–7$ for $H_3IO_6^{2-}$. Assuming Br_2 as the disproportionating substance, we have: $R = 2$, $P = Q = 0$ and then $(R{\cdot}Z_X + P – 2{\cdot}Q){\cdot}C = 2{\cdot}Z_X{\cdot}C$ (4, 9).

The notation $H_pO_qX_r^{+z}{\cdot}n_{pqrz}H_2O$ enables us to distinguish between hydrates of differently charged species, e.g., ClO_2^- and ClO_2, MnO_4^- and MnO_4^{2-}.

Example 5 (Redox System)

Let the subsystem D, of volume V_0 [mL], be composed of N_{D1} molecules of $FeSO_4{\cdot}7H_2O$, N_{D2} molecules of H_2SO_4, and N_{D3} molecules of H_2O, and the subsystem T, of volume V [mL], be composed of N_{T1} molecules of $KMnO_4$ and N_{T2} molecules of H_2O. Addition of T into D is realized in manganometric titration of iron(II) species, where D+T system is formed. One can denote concentrations [mol/L] of the solutes in the subsystems D and T as

$$\frac{N_{D1}}{10^{-3} \cdot N_A \cdot V_0} = C_0, \quad \frac{N_{D2}}{10^{-3} \cdot N_A \cdot V_0} = C_{0a}, \quad \frac{N_{T1}}{10^{-3} \cdot N_A \cdot V} = C \qquad [37a]$$

and the current concentrations [mol/L] of the solutes in D+T system of volume V_0+V:

$$c_0 = \frac{n_0}{V_0 + V} = \frac{10^3 \cdot N_{D1}}{N_A \cdot (V_0 + V)}, \quad c_{0a} = \frac{n_{0a}}{V_0 + V} = \frac{10^3 \cdot N_{D2}}{N_A \cdot (V_0 + V)}, \quad c = \frac{n}{V_0 + V} = \frac{10^3 \cdot N_{T1}}{N_A \cdot (V_0 + V)} \qquad [37b]$$

where:

$$n_0 = C_0 \cdot V_0, \; n_{0a} = C_{0a} \cdot V_0, \; \text{and } n = C \cdot V \qquad [37c]$$

are the numbers of mmoles of the solutes in the subsystems D and T. In D+T system, the following components X_i :

Fe^{2+} (N_1, n_1), $FeOH^+$ (N_2, n_2), $FeSO_4$ (N_3, n_3), Fe^{3+} (N_4, n_4), $FeOH^{2+}$ (N_5, n_5), $Fe(OH)_2^+$ (N_6, n_6), $Fe_2(OH)_2^{4+}$ (N_7, n_7), $FeSO_4^+$ (N_8, n_8), $Fe(SO_4)_2^-$ (N_9, n_9), Mn^{2+} (N_{10}, n_{10}), $MnOH^+$ (N_{11}, n_{11}), $MnSO_4$ (N_{12}, n_{12}), Mn^{3+} (N_{13}, n_{13}), $MnOH^{2+}$ (N_{14}, n_{14}), MnO_4^{2-} (N_{15}, n_{15}), MnO_4^- (N_{16}, n_{16}), HSO_4^- (N_{17}, n_{17}), SO_4^{2-} (N_{18}, n_{18}), H^+ (N_{19}, n_{19}), OH^- (N_{20}, n_{20}) K^+ (N_{21}, n_{21}), and H_2O (N_{22}).

with concentrations [mol/L]

$$[\mathrm{X_i}] = \frac{10^3 \cdot \mathrm{N_i}}{\mathrm{N_A} \cdot (\mathrm{V_0} + \mathrm{V})} \qquad [37d]$$

are considered. On this basis, on can write the balances:

- for H:

$$\mathrm{N_1} \cdot 2\mathrm{n_1} + \mathrm{N_2} \cdot (1 + 2\mathrm{n_2}) + \mathrm{N_3} \cdot 2\mathrm{n_3} + \cdots + \mathrm{N_{18}} \cdot 2\mathrm{n_{18}} + \mathrm{N_{19}} \cdot (1 + 2\mathrm{n_{19}}) + \mathrm{N_{20}} \cdot (1 + 2\mathrm{n_{20}}) + \mathrm{N_{21}} \cdot 2\mathrm{n_{21}} + 2\mathrm{N_{22}} = 14\mathrm{N_{D1}} + 2\mathrm{N_{D2}} + 2\mathrm{N_{D3}} + 2\mathrm{N_{T2}} \qquad [38]$$

- for O:

$$\mathrm{N_1} \cdot \mathrm{n_1} + \mathrm{N_2} \cdot (1 + \mathrm{n_2}) + \mathrm{N_3} \cdot (4 + \mathrm{n_3}) + \cdots + \mathrm{N_8} \cdot (4 + \mathrm{n_8}) + \mathrm{N_9} \cdot (8 + \mathrm{n_9}) + \cdots + \mathrm{N_{18}} \cdot (4 + \mathrm{n_{18}}) + \mathrm{N_{19}} \cdot \mathrm{n_{19}} + \mathrm{N_{20}} \cdot (1 + \mathrm{n_{20}}) + \mathrm{N_{21}} \cdot \mathrm{n_{21}} + \mathrm{N_{22}} = 11\mathrm{N_{D1}} + 4\mathrm{N_{D2}} + \mathrm{N_{D3}} + 4\mathrm{N_{T1}} + \mathrm{N_{T2}} \qquad [39]$$

Multiplying Eq. [39] by 2 and subtracting [38] from the resulting equation gives:

$$\mathrm{N_2} + 8\mathrm{N_3} + \mathrm{N_5} + 2\mathrm{N_6} + 2\mathrm{N_7} + 8\mathrm{N_8} + 16\mathrm{N_9} + \mathrm{N_{11}} + 8\mathrm{N_{12}} + \mathrm{N_{14}} + 8\mathrm{N_{15}} + 8\mathrm{N_{16}} + 7\mathrm{N_{17}} + 8\mathrm{N_{18}} - \mathrm{N_{19}} + \mathrm{N_{20}} = 8\mathrm{N_{D1}} + 6\mathrm{N_{D2}} + 8\mathrm{N_{T1}} \qquad [40]$$

Adding [40] to the rough form of charge balance

$$2\mathrm{N_1} + \mathrm{N_2} + 3\mathrm{N_4} + 2\mathrm{N_5} + \mathrm{N_6} + 4\mathrm{N_7} + \mathrm{N_8} - \mathrm{N_9} + 2\mathrm{N_{10}} + \mathrm{N_{11}} + 3\mathrm{N_{13}} + 2\mathrm{N_{14}} - 2\mathrm{N_{15}} - \mathrm{N_{16}} - \mathrm{N_{17}} - 2\mathrm{N_{18}} + \mathrm{N_{19}} - \mathrm{N_{20}} + \mathrm{N_{T1}} = 0 \qquad [41]$$

we get the equality

$$2\mathrm{N_1} + 2\mathrm{N_2} + 8\mathrm{N_3} + 3\mathrm{N_4} + 3\mathrm{N_5} + 3\mathrm{N_6} + 6\mathrm{N_7} + 9\mathrm{N_8} + 15\mathrm{N_9} + 2\mathrm{N_{10}} + 2\mathrm{N_{11}} + 8\mathrm{N_{12}} + 3\mathrm{N_{13}} + 3\mathrm{N_{14}} + 6\mathrm{N_{15}} + 7\mathrm{N_{16}} + 6\mathrm{N_{17}} + 6\mathrm{N_{18}} = 8\mathrm{N_{D1}} + 6\mathrm{N_{D2}} + 7\mathrm{N_{T1}} \qquad [42]$$

Multiplying the balance for S

$$\mathrm{N_3} + \mathrm{N_8} + 2\mathrm{N_9} + \mathrm{N_{12}} + \mathrm{N_{17}} + \mathrm{N_{18}} = \mathrm{N_{D1}} + \mathrm{N_{D2}} \qquad [43]$$

by 6, then subtracting it from [42] gives the equation

$$2 \cdot (\mathrm{N_1} + \mathrm{N_2} + \mathrm{N_3}) + 3 \cdot (\mathrm{N_4} + \mathrm{N_5} + \mathrm{N_6} + 2\mathrm{N_7} + \mathrm{N_8} + \mathrm{N_9}) + 2 \cdot (\mathrm{N_{10}} + \mathrm{N_{11}} + \mathrm{N_{12}}) + 3 \cdot (\mathrm{N_{13}} + \mathrm{N_{14}}) + 6 \cdot \mathrm{N_{15}} + 7 \cdot \mathrm{N_{16}} = 2 \cdot \mathrm{N_{D1}} + 7 \cdot \mathrm{N_{T1}} \qquad [44]$$

The sum involved with $\mathrm{HSO_4^-}$ and $\mathrm{SO_4^{2-}}$ is cancelled this time. Writing the balances for Fe and Mn and applying Eqs. [37a–d], we have:

$$\mathrm{N_1} + \mathrm{N_2} + \mathrm{N_3} + \mathrm{N_4} + \mathrm{N_5} + \mathrm{N_6} + 2\mathrm{N_7} + \mathrm{N_8} + \mathrm{N_9} = \mathrm{N_{D1}} \qquad [45]$$

$$[\mathrm{Fe^{2+}}] + [\mathrm{FeOH^+}] + [\mathrm{FeSO_4}] + [\mathrm{Fe^{3+}}] + [\mathrm{FeOH^{2+}}] + [\mathrm{Fe(OH)_2^+}] + 2\left[\mathrm{Fe_2(OH)_2^{4+}}\right] + [\mathrm{FeSO_4^+}] + [\mathrm{Fe(SO_4)_2^-}] - \mathrm{C_0V_0}/(\mathrm{V_0} + \mathrm{V}) = 0 \qquad [45a]$$

$$\mathrm{N_{10}} + \mathrm{N_{11}} + \mathrm{N_{12}} + \mathrm{N_{13}} + \mathrm{N_{14}} + \mathrm{N_{15}} + \mathrm{N_{16}} = \mathrm{N_{T1}} \qquad [46]$$

$$[\mathrm{Mn^{2+}}] + [\mathrm{MnOH^+}] + [\mathrm{MnSO_4}] + [\mathrm{Mn^{3+}}] + [\mathrm{MnOH^{2+}}] + \left[\mathrm{MnO_4^{2-}}\right] + [\mathrm{MnO_4^-}] - \mathrm{CV}/(\mathrm{V_0} + \mathrm{V}) = 0 \qquad [46a]$$

Multiplying [45] and [46] by $\mathrm{Z_{Fe}}$ and $\mathrm{Z_{Mn}}$, respectively ($\mathrm{Z_{Fe}} = 26$, $\mathrm{Z_{Mn}} = 25$ – atomic numbers for Fe and Mn), then adding the sides and subtracting [44] from it, we have:

$$(\mathrm{Z_{Fe}} - 2) \cdot (\mathrm{N_1} + \mathrm{N_2} + \mathrm{N_3}) + (\mathrm{Z_{Fe}} - 3) \cdot (\mathrm{N_4} + \mathrm{N_5} + \mathrm{N_6} + 2\mathrm{N_7} + \mathrm{N_8} + \mathrm{N_9}) + (\mathrm{Z_{Mn}} - 2) \cdot (\mathrm{N_{10}} + \mathrm{N_{11}} + \mathrm{N_{12}}) + (\mathrm{Z_{Mn}} - 3)(\mathrm{N_{13}} + \mathrm{N_{14}}) + (\mathrm{Z_{Mn}} - 6) \cdot \mathrm{N_{15}} + (\mathrm{Z_{Mn}} - 7) \cdot \mathrm{N_{16}} = (\mathrm{Z_{Fe}} - 2) \cdot \mathrm{N_{D1}} + (\mathrm{Z_{Mn}} - 7) \cdot \mathrm{N_{T1}} \qquad [47]$$

Dividing the sides of Eq. [47] by $10^{-3} \cdot \mathrm{N_A} \cdot (\mathrm{V_0} + \mathrm{V})$ and applying the formulae [37c] and [37d], we get the equation

$$(\mathrm{Z_{Fe}} - 2) \cdot ([\mathrm{Fe^{2+}}] + [\mathrm{FeOH^+}] + [\mathrm{FeSO_4}]) + (\mathrm{Z_{Fe}} - 3) \cdot ([\mathrm{Fe^{3+}}] + [\mathrm{FeOH_2^+}] + [\mathrm{Fe(OH)^{2+}}] + 2\left[\mathrm{Fe_2(OH)_2^{4+}}\right] + [\mathrm{FeSO_4^+}] + [\mathrm{Fe(SO_4)_2^-}]) + (\mathrm{Z_{Mn}} - 2) \cdot ([\mathrm{Mn^{2+}}] + [\mathrm{MnOH^+}] + [\mathrm{MnSO_4}]) + (\mathrm{Z_{mn}} - 3) \cdot ([\mathrm{Mn^{3+}}] + [\mathrm{MnOH^{2+}}]) + (\mathrm{Z_{Mn}} - 6) \cdot \left[\mathrm{MnO_4^{2-}}\right] + (\mathrm{Z_{Mn}} - 7) \cdot [\mathrm{MnO_4^-}] = ((\mathrm{Z_{Fe}} - 2) \cdot \mathrm{C_0V_0} + (\mathrm{Z_{Mn}} - 7) \cdot \mathrm{CV})/(\mathrm{V_0} + \mathrm{V}) \qquad [48]$$

Equation [48] can also be obtained in a simpler manner (3). In this case, only the elements participating the electron transitions (i.e., Fe and Mn) are considered. Assuming that, at a defined moment of the titration, V mL of C mol/L $\mathrm{KMnO_4}$ was added into $\mathrm{V_0}$ mL of titrand with $\mathrm{FeSO_4}$ ($\mathrm{C_0}$ mol/L) and $\mathrm{H_2SO_4}$ ($\mathrm{C_{0a}}$ mol/L), we have:

$$\mathrm{C_0} \cdot \mathrm{V_0} = 10^3 \cdot \mathrm{N_{D1}}/\mathrm{N_A} \text{ mmoles of Fe and } \mathrm{C} \cdot \mathrm{V} = 10^3 \cdot \mathrm{N_{T1}}/\mathrm{N_A} \text{ mmoles of Mn} \qquad [49]$$

$(\mathrm{Z_{Fe}}–2) \cdot \mathrm{N_{D1}}$ iron–electrons introduced by $\mathrm{FeSO_4 \cdot 7H_2O}$
$(\mathrm{Z_{Mn}}–7) \cdot \mathrm{N_{T1}}$ manganese–electrons introduced by $\mathrm{KMnO_4}$

Then the total number of electrons due to Fe and Mn solutes introduced by $\mathrm{FeSO_4 \cdot 7H_2O}$ and $\mathrm{KMnO_4}$ (Fe+Mn electrons) is

$$(\mathrm{Z_{Fe}} - 2) \cdot \mathrm{N_{D1}} + (\mathrm{Z_{Mn}} - 7) \cdot \mathrm{N_{T1}} = (\mathrm{Z_{Fe}} - 2) \cdot \mathrm{C_0} \cdot \mathrm{V_0} \cdot 10^{-3} \cdot \mathrm{N_A} + (\mathrm{Z_{Mn}} - 7) \cdot \mathrm{C} \cdot \mathrm{V} \cdot 10^{-3} \cdot \mathrm{N_A} \qquad [50]$$

The Fe+Mn electrons are distributed between different Fe and Mn species, i.e., $\mathrm{N_1}$ ions $\mathrm{Fe^{2+}}$ carries $(\mathrm{Z_{Fe}}–2) \cdot \mathrm{N_1}$ Fe-electrons, . . . , $\mathrm{N_{16}}$ ions $\mathrm{MnO_4^-}$ carries $(\mathrm{Z_{Mn}}–7) \cdot \mathrm{N_{16}}$ Mn-electrons.

referred to ith species $\mathrm{X_i}$ (i = 1,. . . ,16) in the mixture of volume $\mathrm{V_0}$+ V into the balance

$$(\mathrm{Z_{Fe}} - 2)(\mathrm{N_1} + \mathrm{N_2} + \mathrm{N_3}) + (\mathrm{Z_{Fe}} - 3)(\mathrm{N_4} + \mathrm{N_5} + \mathrm{N_6} + 2\mathrm{N_7} + \mathrm{N_8} + \mathrm{N_9}) + (\mathrm{Z_{Mn}} - 7)\mathrm{N_{10}} + (\mathrm{Z_2} - 6)\mathrm{N_{11}} + (\mathrm{Z_{Mn}} - 3)(\mathrm{N_{12}} + \mathrm{N_{13}}) + (\mathrm{Z_{Mn}} - 2)(\mathrm{N_{14}} + \mathrm{N_{15}} + \mathrm{N_{16}}) = (\mathrm{Z_{Fe}} - 2) \cdot \mathrm{C_0} \cdot \mathrm{V_0} \cdot 10^{-3} \cdot \mathrm{N_A} + (\mathrm{Z_{Mn}} - 7) \cdot \mathrm{C} \cdot \mathrm{V} \cdot 10^{-3} \cdot \mathrm{N_A} \qquad [51]$$

After transformations, from [51] and [37a–d] one obtains the Eq. [48].

Multiplying [45a] by $Z_{Fe} - 3$, [46a] by $Z_{Mn} - 2$ and subtracting the resulting equation from [48], one obtains another useful form of GEB equation (5, 6, 16)

$$\begin{aligned}&[Fe^{2+}] + [FeOH^{+}] + [FeSO_4] - (5[MnO_4^{-}] + 4\left[MnO_4^{2-}\right] \\ &\quad +[Mn^{3+}] + [MnOH^{2+}]) = (C_0V_0 - 5CV)/(V_0 + V) \quad [48a]\end{aligned}$$

Example 6 (Redox System)

In the paper (17), V_0 mL of titrand (D) was titrated with V mL of titrant (T). The titrand D was composed of: N_a molecules of As_2O_3, N_b molecules of NaOH, N_c molecules of malonic acid ($CH_2C_2O_4H_2$), N_{w1} molecules of H_2O, whereas V mL of T was formed of: N_d molecules of I_2, N_e molecules of KI, and N_{w2} molecules of H_2O.

In the titration, one can distinguish two steps. On the first step, at $V < V_{eq}$ (V_{eq}—equivalence volume) the main reactions are:

$$HAsO_2 + I_2(I_3^-) + 2H_2O = H_2AsO_4^- + 2I^-(3I^-) + 3H^+ \quad [52]$$

$$HAsO_2 + I_2(I_3^-) + 2H_2O = HAsO_4^{2-} + 2I^-(3I^-) + 4H^+ \quad [53]$$

On the second step, at $V \geq V_{eq}$, malonate species are oxidized in kinetic reactions:

$$\begin{aligned}&CH_2C_2O_4H_i^{-2+i} + I_2(I_3^-) \\ &\quad = CHIC_2O_4H_j^{-2+j} + (1 + i - j)H^+ + I^-(2I^-) \quad [54]\end{aligned}$$

At $V < V_{eq}$, iodine is not consumed in reaction [54].

Applying the notation similar to one presented in Examples 3 and 5, one can characterize the composition of D+T system, with volume V_0+ V mL, as follows:

H^+ (n_1, N_1), OH^- (n_2, N_2), H_2O (N_3), $HAsO_2$ (n_4, N_4), AsO_2^- (n_5, N_5), H_3AsO_4 (n_6, N_6), $H_2AsO_4^-$ (n_7, N_7), $HAsO_4^{2-}$ (n_8, N_8), AsO_4^{3-} (n_9, N_9), I^- (n_{10}, N_{10}), I_3^- (n_{11}, N_{11}), I_2 (n_{12}, N_{12}), HIO (n_{13}, N_{13}), IO^- (n_{14}, N_{14}), HIO_3 (n_{15}, N_{15}), IO_3^- (n_{16}, N_{16}), H_5IO_6 (n_{17}, N_{17}), $H_4IO_6^-$ (n_{18}, N_{18}), $H_3IO_6^{2-}$ (n_{19}, N_{19}), K^+ (n_{20}, N_{20}), Na^+ (n_{21}, N_{21}), $CH_2C_2O_4H_2$ (n_{22}, N_{22}), $CH_2C_2O_4H^-$ (n_{23}, N_{23}), $CH_2C_2O_4^{2-}$ (n_{24}, N_{24}), $CHIC_2O_4H_2$ (n_{25}, N_{25}), $CHIC_2O_4H^-$ (n_{26}, N_{26}), $CHIC_2O_4^{2-}$ (n_{27}, N_{27}).

Then one can formulate the elemental balances for H and O:

$$\begin{aligned}&N_1(1 + 2n_1) + N_2(1 + 2n_2) + 2N_3 + N_4(1 + 2n_4) \\ &\quad + N_5 \cdot 2n_5 + N_6(3 + 2n_6) + N_7(2 + 2n_7) + N_8(1 + 2n_8) \\ &\quad + N_9 \cdot 2n_9 + N_{10} \cdot 2n_{10} + N_{11} \cdot 2n_{11} + N_{12} \cdot 2n_{12} \\ &\quad + N_{13} \cdot (1 + 2n_{13}) + N_{14} \cdot 2n_{14} + N_{15} \cdot (1 + 2n_{15}) \\ &\quad + N_{16} \cdot 2n_{16} + N_{17}(5 + 2n_{17}) + N_{18}(4 + 2n_{18}) \\ &\quad + N_{19} \cdot (3 + 2n_{19}) + N_{20} \cdot 2n_{20} + N_{21} \cdot 2n_{21} \\ &\quad + N_{22} \cdot (4 + 2n_{22}) + N_{23} \cdot (3 + 2n_{23}) + N_{24} \cdot (2 + 2n_{24}) \\ &\quad + N_{25} \cdot (3 + 2n_{25}) + N_{26} \cdot (2 + 2n_{26}) + N_{27} \cdot (1 + 2n_{27}) \\ &\quad = N_b + 4N_c + 2N_{w1} + 2N_{w2} \qquad [55]\end{aligned}$$

$$\begin{aligned}&N_1 \cdot n_1 + N_2(1 + n_2) + N_3 + N_4(2 + n_4) + N_5(2 + n_5) \\ &\quad + N_6(4 + n_6) + N_7(4 + n_7) + N_8(4 + n_8) + N_9(4 + n_9) \\ &\quad + N_{10} \cdot n_{10} + N_{11} \cdot n_{11} + N_{12} \cdot n_{12} + N_{13}(1 + n_{13}) \\ &\quad + N_{14}(1 + n_{14}) + N_{15}(3 + n_{15}) + N_{16}(3 + n_{16}) \\ &\quad +N_{17}(6 + n_{17}) + N_{18}(6 + n_{18}) + N_{19}(6 + n_{19}) \\ &\quad + N_{20} \cdot n_{20} + N_{21} \cdot n_{21} + N_{22}(4 + n_{22}) + N_{23}(4 + n_{23}) \\ &\quad + N_{24}(4 + n_{24}) + N_{25}(4 + n_{25}) + N_{26}(4 + n_{26}) \\ &\quad + N_{27}(4 + n_{27}) = 3N_a + N_b + 4N_c + N_{w1} + N_{w2} \qquad [56]\end{aligned}$$

respectively. Subtracting [55] from [56] multiplied by 2, we have

$$\begin{aligned}&-N_1 + N_2 + 3N_4 + 4N_5 + 5N_6 + 6N_7 + 7N_8 + 8N_9 \\ &\quad + N_{13} + 2N_{14} + 5N_{15} + 6N_{16} + 7N_{17} + 8N_{18} + 9N_{19} \\ &\quad + N_{22} + 5N_{23} + 6N_{24} + 5N_{25} + 6N_{26} + 7N_{27} \\ &\quad = 6N_a + N_b + 4N_c \qquad [57]\end{aligned}$$

Adding [57] to the primary forms of charge balance and other (arranged) elemental balances:

$$\begin{aligned}&N_1 - N_2 - N_5 - N_7 - 2N_8 - 3N_9 - N_{10} - N_{11} - N_{14} \\ &\quad - N_{16} - N_{18} - 2N_{19} + N_{20} + N_{21} - N_{23} \\ &\quad - 2N_{24} - N_{26} - 2N_{27} = 0 \\ &N_b = N_{21} \\ &N_e = N_{20} \\ &N_{10} + 3N_{11} + 2N_{12} + N_{13} + N_{14} + N_{15} + N_{16} + N_{17} + N_{18} \\ &\quad + N_{19} + N_{25} + N_{26} + N_{27} = 2N_d + N_e \qquad [58] \\ &4N_c = 4N_{22} + 4N_{23} + 4N_{24} + 4N_{25} + 4N_{26} + 4N_{27}\end{aligned}$$

gives the balance

$$\begin{aligned}&3(N_4 + N_5) + 5(N_6 + N_7 + N_8 + N_9) + 2(N_{11} + N_{12} + N_{13} \\ &\quad + N_{14}) + 6(N_{15} + N_{16}) + 8(N_{17} + N_{18} + N_{19}) \\ &\quad + 2(N_{25} + N_{26} + N_{27}) = 6N_a + 2N_d \qquad [59]\end{aligned}$$

Let us denote atomic numbers: Z_{As} (= 33) for As and Z_i (= 53) for I. Multiplying the sides of [58] by Z_i+ 1, and the sides of balance for As

$$N_4 + N_5 + N_6 + N_7 + N_8 + N_9 = 2N_a \qquad [60]$$

by Z_{As}, and combining the resulting equations with [59], we get the equation

$$\begin{aligned}&(Z_{As} - 3)(N_4 + N_5) + (Z_{As} - 5)(N_6 + N_7 + N_8 + N_9) \\ &\quad + (Z_I + 1)N_{10} + (3Z_I + 1)N_{11} + 2Z_IN_{12} \\ &\quad + (Z_I - 1)(N_{13} + N_{14}) + (Z_I - 5)(N_{15} + N_{16}) \\ &\quad + (Z_I - 7)(N_{17} + N_{18} + N_{19}) + (Z_I - 1)(N_{25} + N_{26}+N_{27}) \\ &\quad = 2(Z_{As} - 3)N_a + 2Z_IN_d + (Z_I + 1)N_e \qquad [61]\end{aligned}$$

Dividing the sides of [61] by $10^{-3}N_A(V_0$+ V) and denoting:

$$N_a/N_A = 10^{-3}C_0V_0,\ N_d/N_A = 10^{-3}CV,\ N_e/N_A = 10^{-3}C_IV$$

we get the electron balance (GEB)

$$\begin{aligned}&(Z_{As}-3)([HAsO_2]+[AsO_2^-])+(Z_{As}-5)\big([H_3AsO_4]\\&\quad+[H_2AsO_4^-]+\left[HAsO_4^{2-}\right]+\left[AsO_4^{3-}\right]\big)+(Z_I+1)[I^-]\\&\quad+(3Z_I+1)[I_3^-]+2Z_I[I_2]+(Z_I-1)([HIO]+[IO^-])\\&\quad+(Z_I-5)([HIO_3]+[IO_3^-])+(Z_I-7)\big([H_5IO_6]\\&\quad+[H_4IO_6^-]+\left[H_3IO_6^{2-}\right]\big)+(Z_I-1)([CHIC_2O_4H_2]\\&\quad+\left[CHIC_2O_4H^-\right]+[CHIC_2O_4^{2-}])=(2(Z_{As}-3)C_0V_0\\&\quad+2Z_ICV+(Z_I+1)C_IV)/(V_0+V)\qquad[62]\end{aligned}$$

Combining the resulting equation with concentration balances for As and I:

$$\begin{aligned}&[HAsO_2]+[AsO_2^-]+[H_3AsO_4]+[H_2AsO_4^-]\\&\quad+\left[HAsO_4^{2-}\right]+\left[AsO_4^{3-}\right]=2C_0V_0/(V_0+V)\qquad[63]\\&[I^-]+3[I_3^-]+2[I_2]+[HIO]+[IO^-]+[HIO_3]+[IO_3^-]\\&\quad+[H_5IO_6]+[H_4IO_6^-]+\left[H_3IO_6^{2-}\right]+\left[CHIC_2O_4H_2\right]\\&\quad+[CHIC_2O_4H^-]+\left[CHIC_2O_4^{2-}\right]\\&\quad=(2CV+C_IV)/(V_0+V)\qquad[64]\end{aligned}$$

multiplied by $Z_{As}-5$ and Z_i+1, respectively, we get the equation

$$\begin{aligned}&[HAsO_2]+[AsO_2^-]-\big([I_3^-]+[I_2]+[HIO]+[IO^-]\\&\quad+3([HIO_3]+[IO_3^-])+4\big([H_5IO_6]+[H_4IO_6^-]\\&\quad+\left[H_3IO_6^{2-}\right]\big)+[CHIC_2O_4H_2]+[CHIC_2O_4H^-]\\&\quad+\left[CHIC_2O_4^{2-}\right]\big)=(2C_0V_0-CV)/(V_0+V)\qquad[65]\end{aligned}$$

At $V < V_{eq}$, one can assume that $[CHIC_2O_4H_2] = [CHIC_2O_4H^-] = [CHIC_2O_4^{2-}]) = 0$. This fact was confirmed experimentally (17). The titration curves, consisting of rectilinear lines intersecting at the equivalence volume V_{eq}, are presented in Fig. 2. These curves were obtained at different rates of the titrant addition. As we see, the curves overlap at $V < V_{eq}$ and fork at $V > V_{eq}$. At $V < V_{eq}$, iodine is consumed in a fast reaction with $HAsO_2$ as the main As(III) species in this system at pH ca. 6. The main products of this reaction are: $H_2AsO_4^-$ and $HAsO_4^{2-}$. The fraction $[H_2AsO_4^-]/[HAsO_4^{2-}]$ varies from ca. 4.6–10 within the $0 \le V \le V_{eq}$ interval, so then the main and accompanying reactions are expressed by reactions [52] and [53]. The number of protons generated during these reactions exceeds three per molecule of $HAsO_2$. The rate of these reactions is apparently greater than for reactions involved with oxidation of malonic acid species (Eq. 54). The overlapping at $V < V_{eq}$ and the fact that the equivalence point occurs at the stoichiometric point, testifies in favor of the opinion that I_2 and I_3^- are not consumed by malonate species at $V < V_{eq}$. Different shape of the curves at $V > V_{eq}$, where As(III) species does not already exist, testify on account of the kinetic course of reactions [54] in this V-interval. The reactions of iodine species with the components of D can therefore be considered, respectively, as thermodynamic for $V < V_{eq}$ (where malonate species act only as buffering agents) or kinetic for $V > V_{eq}$ (where malonate species act also as reducing agents).

OPTIMIZING PROCEDURE—GENERAL REMARKS

The material balances, related to a dynamic system and realized according to titrimetric mode, can be written as a set of algebraic equations $Fi = F_i(\mathbf{x}(V)) = 0$, where $\mathbf{x}(V) = [x_1(V), \ldots, x_n(V)]^T$ is the vector of fundamental variables $x_i = x_i(V)$ (scalars) related to a particular V–value, i.e., volume of titrant added. The number (n) of variables is equal to the number of the balances. At defined V–value, only one vector, $\mathbf{x} = \mathbf{x}(V)$, exists that turns the set of algebraic expressions $F_i(\mathbf{x}(V))$ to zero, i.e., $F_i(\mathbf{x}(V)) = 0$ (i = 1,. . . ,n) and the sum of squares

$$SS = SS(V) = \sum_{i=1}^{n}[F_i(\mathbf{x}(V))]^2 \qquad [66]$$

be equal zero, i.e.,

$$SS = SS(V) = \sum\nolimits_{i=1}^{n}[F_i(\mathbf{x}(V))]^2 = 0 \qquad [67]$$

for any V–value. If $\mathbf{x}_s(V) \neq \mathbf{x}(V)$, one can expect that $SS = SS(V) = \sum_{i=1}^{n}[F_i(\mathbf{x}_s(V))]^2 > 0$.

Let $\mathbf{x}_s(V)$ be a vector of starting (s) values for fundamental (independent) variables related to a particular V–value. The searching of $\mathbf{x}(V)$ vectors at different V–values where $F_i(\mathbf{x}(V)) = 0$ (i = 1,. . . , n) is made according to iterative computer programs (18), e.g., one with the Marquardt–Levenberg algorithm applied. Another program applied by us for this purpose is the MINUIT computer program, involving simplex and gradient searching procedures. The searching procedure satisfies the requirements put on optimal $\mathbf{x}(V)$ values provided that SS value Eq. [66] is lower than a pre–assumed, sufficiently low δ–value, i.e.,

$$SS = \sum_{i=1}^{n}(Fi)^2 = \sum_{i=1}^{n}[F_i(\mathbf{x}(V))]^2 < \delta \qquad [68]$$

However, the iterative computer programs are (generally) designed for the curve–fitting procedures where the degree of fitting of a curve to experimental points is finite. In this case, the criterion of optimization is based on differences SS(N+1) – SS(N) between two successive (Nth and N+1th) approximations of SS–value, i.e.,

$$|SS(N+1) - SS(N)| < \delta \qquad [69]$$

at a sufficiently low δ–value, $\delta > 0$, e.g., $\delta = 10^{-14}$. However, one should take into account that the condition [69] can be fulfilled at local (l) minimum $\mathbf{x}_l(V)$, distant from the global minimum. It can happen if the starting values $\mathbf{x}_s(V)$ are too distant from the true value $\mathbf{x}(V)$ where the equality [67] is fulfilled. In this case, one should try (repeat) the calculations for new $\mathbf{x}_s(V)$ values guessed.

The choice of δ–value depends on the scale of analytical concentrations considered. To “equalise” the requirements put on particular balances, it is advised (10) to apply 'normalized' balances Fin, e.g., to divide the related balance by the starting (analytical) concentration C_i involved in this balance, i.e., to write $\mathrm{Fin} = \mathrm{Fi}/C_i$, and then to check the $\mathbf{x}(V)$ values for

$$\mathrm{SSn} = \sum_{i=1}^{n} (\mathrm{Fin})^2 \qquad [70]$$

In all simulated titrations, the following regularities are complied:

1. The variables x(i) are introduced as the (negative) powers of 10 (as the base number); for any $[X] > 0$ one can write $[X] \equiv 10^{\log[X]} = 10^{-pX}$, where $pX = -\log[X]$. One should be noted that $[X] > 0$ for any real pX value, $pX \in \Re$. It particularly refers to protons (H^+) and electrons (e^-), namely

$$[H^+] = 10^{-pH} \qquad [71]$$

$$[e^-] = 10^{-E/\vartheta} \qquad [72]$$

   where (3,9,10)

$$\vartheta = RT/F \cdot \ln 10 = 0.0591 \ \ \mathrm{V\ at\ 25^\circ C} \qquad [73]$$

   for ideal indicator electrode.
2. The changes in the system are made according to titrimetric mode, with volume V taken as the steering variable; the titration is considered as a kind of dynamic process, realized in a *quasistatic* manner under isothermal conditions.
3. It is advisable to refer the fundamental variables to the species whose concentrations predominate at the start for calculations.

Generally, the parameter V is the steering variable in material balances. The optimizing calculation starts at the V–value, V = V(start), that appears to be "comfortable" from the user's viewpoint, where the starting $x_{is}(V)$ values are guessed. Then the optimization is realized, with a negative step put on the V–variable, up to V = V(begin) close to zero value. The possible changes in the phase composition within the interval [V(begin), V(start)] should also be taken into account. The proper optimization procedure starts from the V(begin) value with positive step assumed up to the final value, V(end). All possible changes in the phase composition should be taken into account, both in the [V(start), V(begin)] and [V(begin), V(end)] intervals. It particularly refers to formation/disappearance of a solid phase(s) or a change in equilibrium solid phase (13). For this purpose, the expressions identical with the forms of the corresponding solubility products should be "peered" during the simulated titration. The solid phase may not be involved with the "classical" solubility product but it may result from a limited solubility of a substance considered, e.g., iodine.

All calculations done in this paper were performed with use of iterative (MATLAB, MINUIT) computer programs.

ASCORBINOMETRIC TITRATION OF IODATE AS AN EXAMPLE OF RESOLUTION OF ANALYTICAL SYSTEM

Let us consider the titration of V_0 mL of the solution containing $\mathrm{KIO_3}$ (C_0 mol/L) + HCl (C_a mol/L) + $\mathrm{H_2SeO_3}$ (C_{Se} mol/l) + $\mathrm{HgCl_2}$ (C_{Hg} mol/L) with V mL of C mol/L ascorbic acid ($\mathrm{C_6H_8O_6}$); $\mathrm{H_2SeO_3}$ has been applied as the catalyst. As has been stated in (2), the shapes of $E = E(\Phi)$ and $pH = pH(\Phi)$ functions depend on the presence/absence of $\mathrm{HgCl_2}$ in the titrand (solution titrated). The related effects can be explained on the basis of dynamic speciation curves $\log[X_i] = f_i(\Phi)$ plotted for different species X_i. In (11), the possibility of oxidation of $\mathrm{Cl^-}$ has been taken into account. Presently, the Se(IV) oxidation and Hg(II) reduction are also considered.

The species considered in this system are involved in the set of balances, consisting of:

- concentration balances:

$$\begin{aligned}
F1 = {} & [\mathrm{I^{-1}}] + 3[\mathrm{I_3^-}] + 2([\mathrm{I_2}] + \alpha \cdot [\mathrm{I_2}]) + [\mathrm{HIO}] + [\mathrm{IO^-}] \\
& + [\mathrm{HIO_3}] + [\mathrm{IO_3^-}] + [\mathrm{H_5IO_6}] + [\mathrm{H_4IO_6^-}] \\
& + \left[\mathrm{H_3IO_6^{2-}}\right] + [\mathrm{HgI^+}] + 2[\mathrm{HgI^2}] + 3[\mathrm{HgI_3^-}] \\
& + 4\left[\mathrm{HgI_4^{2-}}\right] + [\mathrm{ICl}] + [\mathrm{ICl_2^-}] + 2[\mathrm{I_2Cl^-}] \\
& - C_0V_0/(V_0 + V) = 0 \qquad [74]
\end{aligned}$$

$$\begin{aligned}
F2 = {} & [\mathrm{Hg^{2+}}] + [\mathrm{HgOH^+}] + [\mathrm{Hg(OH)_2}] + [\mathrm{HgCl^+}] \\
& + [\mathrm{HgCl_2}] + [\mathrm{HgCl_3^-}] + [\mathrm{HgCl_4^{2-}}] + [\mathrm{HgI^+}] \\
& + [\mathrm{HgI_2}] + [\mathrm{HgI_3^-}] + \left[\mathrm{HgI_4^{2-}}\right] + 2g \cdot ([\mathrm{Hg_2^{2+}}] \\
& + [\mathrm{Hg_2OH^+}]) - C_{Hg}V_0/(V_0 + V) = 0 \qquad [75]
\end{aligned}$$

$$\begin{aligned}
F3 = {} & [\mathrm{C_6H_8O_6}] + \left[\mathrm{C_6H_7O_6^-}\right] + [\mathrm{C_6H_6O_6^{2-}}] + [\mathrm{C_6H_6O_6}] \\
& - CV/(V_0 + V) = 0 \qquad [76]
\end{aligned}$$

$$\begin{aligned}
F4 = {} & [\mathrm{Cl^-}] + 2[\mathrm{Cl^2}] + [\mathrm{HClO}] + [\mathrm{ClO^-}] + [\mathrm{HClO_2}] \\
& + [\mathrm{ClO_2^-}] + [\mathrm{ClO_2}] + [\mathrm{ClO_3^-}] + [\mathrm{ClO_4^-}] + [\mathrm{ICl}] \\
& + 2[\mathrm{ICl_2^-}] + [\mathrm{I_2Cl^-}] + [\mathrm{HgCl^+}] + 2[\mathrm{HgCl_2}] \\
& + 3[\mathrm{HgCl_3^-}] + 4\left[\mathrm{HgCl_4^{2-}}\right] \\
& - (2C_{Hg} + C_a)V_0/(V_0 + V) = 0 \qquad [77]
\end{aligned}$$

$$\begin{aligned}
F5 = {} & [\mathrm{H_2SeO_3}] + [\mathrm{HSeO_3^-}] + \left[\mathrm{SeO_3^{2-}}\right] + \beta \cdot ([\mathrm{HSeO_4^-}] \\
& + \left[\mathrm{SeO_4^{2-}}\right]) - C_{Se}V_0/(V_0 + V) = 0 \qquad [78]
\end{aligned}$$

- charge balance:

$$\begin{aligned}
F6 = {} & C_0V_0/(V_0 + V) + [\mathrm{H^+}] - [\mathrm{OH^-}] - [\mathrm{I^-}] - [\mathrm{I_3^-}] \\
& - [\mathrm{IO^-}] - [\mathrm{IO_3^-}] - \left[\mathrm{H_4IO_6^-}\right] - 2\left[\mathrm{H_3IO_6^{2-}}\right] - [\mathrm{Cl^-}] \\
& - [\mathrm{ClO^-}] - [\mathrm{ClO_2^-}] - [\mathrm{ClO_3^-}] - \left[\mathrm{ClO_4^-}\right] - \left[\mathrm{ICl_2^-}\right] \\
& - [\mathrm{I_2Cl^-}] + 2[\mathrm{Hg^{2+}}] + [\mathrm{HgOH^+}] + \gamma \cdot (2\left[\mathrm{Hg_2^{2+}}\right] \\
& + [\mathrm{Hg_2OH^+}]) + [\mathrm{HgCl^+}] - \left[\mathrm{HgCl_3^-}\right] - 2\left[\mathrm{HgCl_4^{2-}}\right] \\
& + [\mathrm{HgI^+}] - \left[\mathrm{HgI_3^-}\right] - 2\left[\mathrm{HgI_4^{2-}}\right] - \left[\mathrm{C_6H_7O_6^-}\right] \\
& - 2\left[\mathrm{C_6H_6O_6^{2-}}\right] - \beta \cdot (\left[\mathrm{HSeO_4^-}\right] + 2[\mathrm{SeO_4^{2-}}]) \\
& - \left[\mathrm{HSeO_3^-}\right] - 2\left[\mathrm{SeO_3^{2-}}\right] = 0 \qquad [79]
\end{aligned}$$

- and electron balance

$$\begin{aligned}
\mathrm{F7} = {} & (Z_1+1)[I^-] + (3Z_1+1)[I_3^-] + 2Z_1([I_2] + \alpha\cdot[\mathbf{I_2}]) + (Z_1-1)([HIO]+[IO^-]) + (Z_1-5)([HIO_3]+[IO_3^-]) + \\
& (Z_1-7)([H_5IO_6]+[H_4IO_6^-]+[H_3IO_6^{2-}]) + (Z_2-2)([Hg^{2+}]+[HgOH^+]+[Hg(OH)_2]) + \\
& (Z_2-2+Z_1+1)[HgI^+] + (Z_2-2+2(Z_1+1))[HgI_2] + (Z_2-2+3(Z_1+1))[HgI_3^-] + \\
& (Z_2-2+4(Z_1+1))\left[HgI_4^{2-}\right] + 2\gamma\cdot(Z_2-1)\left(\left[Hg_2^{2+}\right]+\left[Hg_2OH^+\right]\right) + \\
& Z_3\left([C_6H_8O_6]+[C_6H_7O_6^-]+\left[C_6H_6O_6^{2-}\right]\right) + (Z_3-2)[C_6H_6O_6] + (Z_4+1)[Cl^-] + 2Z_4[Cl^2] + \\
& (Z_4-1)([HClO]+[ClO^-]) + (Z_4-3)([HClO_2]+[ClO_2^-]) + (Z_4-4)[ClO_2] + (Z_4-5)[ClO_3^-] + \\
& (Z_4-7)[ClO_4^-] + (Z_1+Z_4)[ICl] + (Z_1+2(Z_4+1))[ICl_2^-] + (2Z_1+Z_4+1)[I_2Cl^-] + (Z_2-2+Z_4+1)[HgCl^+] + \\
& (Z_2-2+2(Z_4+1))[HgCl_2] + (Z_2-2+3(Z_4+1))[HgCl_3^-] + (Z_2-2+4(Z_4+1))[HgCl_4^{2-}] + \\
& (Z_5-4)\{[H_2SeO_3]+[HSeO_3^-]+\left[SeO_3^{2-}\right]) + \beta\cdot(Z_5-6)\left(\left[HSeO_4^-\right]+\left[SeO_4^{2-}\right]\right) \\
& -((Z_1-5)C_0V_0 + (Z_2-2+2(Z_4+1))C_{Hg}V_0 + Z_3CV + (Z_4+1)C_aV_0 + (Z_5-4)C_{Se}V_0)/(V_0+V) = 0 \qquad [80]
\end{aligned}$$

The following terms were introduced there:

- $\alpha = 1$, valid under the assumption that solid iodine ($\mathbf{I}_2$) is present in the system considered; $\alpha = 0$, for a system not saturated against solid iodine;
- $\beta = 1$, referring to the case where Se(VI) species were involved; at $\beta = 0$, the Se(VI) species are omitted;
- $\gamma = 1$, referring to the case where Hg(I) species were involved; at $\gamma = 0$, the Hg(I) species are omitted.

All attainable physicochemical knowledge on the system considered is involved in the relations for the corresponding equilibrium constants:

$$\begin{aligned}
& [I_2] = [I^-]^2\cdot 10^{2A(E-0.62)},\ [I_3^-] = [I^-]^3\cdot 10^{2A(E-0.545)},\ [IO^-] = [I^-]\cdot 10^{2A(E-0.49)+2pH-28},\ [IO_3^-] = [I^-]\cdot 10^{6A(E-1.08)+6pH}, \\
& [HIO] = 10^{10.6}\cdot[H^+][IO^-],\ [HIO_3] = 10^{0.79}\cdot[H^+][IO_3^-],\ [H_5IO_6] = [I^-]\cdot 10^{8A(E-1.26)+7pH}, \\
& [H_4IO_6^-] = 10^{pH-3.3}\cdot[H_5IO_6],\ [H_3IO_6^{2-}] = [I^-]\cdot 10^{8A(E-0.37)+9pH-126}, \\
& [C_6H_6O_6] = [C_6H_8O_6]\cdot 10^{2A(E-0.39)+2pH},\ [C_6H_8O_6] = [C_6H_7O_6^-]\cdot 10^{4.21-pH},\ [C_6H_8O_6] = [C_6H_6O_6^{2-}]\cdot 10^{15.78-2pH}, \\
& [I_2] = [ICl]^2\cdot 10^{-2A(E-1.105)+2pCl},\ [I_2Cl^-] = [I_2]\cdot 10^{0.2-pCl},\ [ICl_2^-] = [ICl]\cdot 10^{2.2-pCl}, \\
& [SeO_4^{2-}] = [H_2SeO_3]\cdot 10^{2A(E-1.139)+4pH},\ [H_2SeO_3] = 10^{2.62}\cdot[H^+][HSeO_3^-],\ [H_2SeO_3] = 10^{10.94}\cdot[H^+]^2[SeO_3^{2-}],\ [HSeO_4^-] \\
& \quad = 10^{1.88}\cdot[H^+][SeO_4^{2-}],\ [Hg_2^{2+}] = [Hg^{2+}]^2\cdot 10^{-2A(E-0.92)},\ [HgOH^+] = [Hg^{2+}]\cdot 10^{pH-3.7}, \\
& [Hg_2OH^+] = 10^{10.4}[Hg_2^{2+}][OH^-],\ [Hg(OH)_2] = [Hg^{2+}]\cdot 10^{2pH-6.3},\ [HgCl^+] = [Hg^{2+}]\cdot 10^{6.74-pCl}, \\
& [HgCl_2] = [Hg^{2+}]\cdot 10^{13.22-2pCl},\ [HgCl_3^-] = [Hg^{2+}]\cdot 10^{14.07-3pCl},\ [HgCl_4^{2-}] = [Hg^{2+}]\cdot 10^{15.07-4pCl}, \\
& [HgI^+] = [Hg^{2+}]\cdot 10^{12.87-pI},\ [HgI_2] = [Hg^{2+}]\cdot 10^{23.8-2pI},\ [HgI_3^-] = [Hg^{2+}]10^{27.6-3pI},\ [HgI_4^{2-}] = \\
& [Hg^{2+}]10^{29.6-4pI},\ [Cl_2] = 10^{2A(E-1.359)-2pCl},\ [ClO^-] = 10^{2A(E-0.88)+2pH-pCl-28},\ [HClO] = 10^{7.3}[H^+][ClO^-], \\
& [ClO_2^-] = 10^{4A(E-0.77)+4pH-pCl-56},\ [HClO_2] = 10^{1.97}[H^+][ClO_2^-],\ [ClO_2] = 10^{5A(E-1.5)+4pH-pCl}, \\
& [ClO_3^-] = 10^{6A(E-1.45)+6pH-pCl},\ [ClO_4^-] = 10^{8A(E-1.38)+8pH-pCl} \qquad [81]
\end{aligned}$$

where pCl = –log[Cl$^-$], pI = –log[I$^-$], A = 1/ϑ (Eq. [73]).

The changes of E and pH during the titration are specified in Figs. 3 and 4. The plots presented there were obtained under assumption that: (a) Se(VI) and Hg(I) species were not involved in the related balances ($\beta = \gamma = 0$); (b) only Se(VI) species are involved ($\gamma = 0$); (c) only Hg(I) species are involved ($\beta = 0$); and (d) both Se(VI) and Hg(I) species are involved ($\beta = \gamma = 1$).

It should be noticed that Se(VI) and/or Hg(I) species involved in the model do not shift the position of $\Phi = \Phi_{eq}$–value where a high jump on the curve occurs.

Comparing the curves in Fig. 4 with the related experimental curves (19), one can state that $\beta = \gamma = 0$, i.e., the system is in a metastable state with respect to Se(VI) and Hg(I).

The optimization procedure can be applied to mono- and poly-phase, batch [e.g., (3)] and dynamic systems.

REMARKS ON MATERIAL BALANCES

The set of material balances, consisting of charge balance, concentration balance(s) and electron balance, involves all species existing really in a redox system. Assuming that the term "material balance" is ascribed to the balance involving at least two species, one can state that the number of balances equals the number of fundamental variables. For example, in the system where V_0 mL of $FeSO_4$+ H_2SO_4 solution is titrated with V mL of C mol/L $KMnO_4$, the balance for potassium ions involves only one species, $[K^+] = CV/(V_0+V)$; it can be then immediately inserted into the charge balance. In other words, the value for $[K^+]$ is not optimized; its value is accurately defined at any stage of the titration.

The material balances form the linearly independent set of algebraic equations, consisting of Q concentration balances, one charge balance, and one electron balance; the electron balance is ascribed to redox systems. Summarizing, one can state that:

- Non–redox systems are described by $n = Q + 1$ balances, i.e., Q concentration balances and one charge balance.
- Redox systems are described by $n = Q + 2$ balances, i.e., Q concentration balances, one charge balance and one electron balance.

Owing to the interdependency stated for some material balances and the linear independency required for the balances formulated for calculation purposes, one should discipline the term "concentration balance" referred to electrolytic systems, with aqueous solution involved. Namely:

- Concentration balances are referred to the species introduced into water or forming a mono- or polyphase system with water;
- Concentration balances for H and O are not formulated—except the cases where the substance introduced involves or is able to form the species with oxidation degrees different from +1 for H and –2 for O; it particularly concerns the species such as H_2O_2, O_2, F_2 and H_2, hydrides, and metallic Na;
- Omission of the products of the related reaction (e.g., oxidation, reduction, complexation) in the related balances is tantamount with the assumption that the related reaction does not occur; this omission is immediately involved with metastable state and potential activity or inactivity of the related species in the system in question;
- Concentration balances are not tantamount with elemental balances (see Section 7);
- Boundaries of the system considered are limited to condensed (liquid, solid) phases.

Generally, all the balances should be formed with great intuition and care, with all information concerning kinetics of the related (potential) transformations involved.

In the systems considered above, water did not participate as an active (reducing or oxidizing) reagent. An example with H_2O as the reducing agent is the system obtained after introducing gaseous F_2 into water. Assuming the existence of the following species: F_2, F_2O, HF, H_2F_2, F^-, O_2, O_3, H_2O_2, HO_2^-, O_2^-, H^+, OH^-, and H_2O, from the balances for H and O one obtains the equality

$$[H^+] - [OH^-] + [HF] + 2[H_2F_2] = 2[F_2O] + 4[O_2] + 6[O_3] + 2[H_2O_2] + 3[HO_2^-] + 4[O_2^-] \quad [82]$$

Combining [82] with the related charge balance, one obtains another form of the electron balance

$$[HF] + [F^-] + 2[H_2F_2] = 2[F_2O] + 4[O_2] + 6[O_3] + 2[H_2O_2] + 2[HO_2^-] + 3[O_2^-] \quad [83]$$

GEB, in context with GATES, enables one to proceed full speciation analysis of one- and two-phase systems, also for liquid-liquid extraction systems. It is a new, much more advantageous proposal against the resolutions known hitherto, particularly represented by Pourbaix diagrams (20), with only the predominant species represented as area on a two-dimensional (2-D) plane with coordinates (pH, E). The Pourbaix diagrams appear to be completely destroyed (and then useless) if a new component, e.g., complexing agent, is introduced. In this respect, GATES provides a new quality of knowledge, incomparably better than one offered by Pourbaix diagrams. According to GATES, it is possible to arrange any system of entrance substances and, after due calculations, to obtain any relationship—also in graphical (2-D or 3-D) presentation.

SOME PITFALLS IN THE BALANCES FORMULATION

In the case of addition of V mL of Na_2CO_3 (C) into V_0 mL of $H_2C_2O_4$ (C_0), the concentration balances for carbonate and oxalate species should be formulated separately, i.e.,

$$[H_2C_2O_4] + [HC_2O_4^-] + \left[C_2O_4^{2-}\right] = C_0V_0/(V_0 + V)$$
$$\text{and} \quad [H_2CO_3] + [HCO_3^-] + \left[CO_3^{2-}\right] = CV/(V_0 + V) \quad [84]$$

However, if V_0 mL of $H_2C_2O_4$ (C_0) solution is titrated with V mL $KMnO_4$ (C) in acidic (H_2SO_4) media, oxalate and carbonate species enter the same concentration balance (11, 12)

$$2[H_2C_2O_4] + 2[HC_2O_4^-] + 2\left[C_2O_4^{2-}\right] + [H_2CO_3] + [HCO_3^-] + \left[CO_3^{2-}\right] - 2C_0V_0/(V_0 + V) = 0 \quad [85]$$

Some further limitations are involved with factual disability of diluted solutions of some species (e.g., ClO_4^-, SO_4^{2-}) for oxidation of other species formed by the same element (e.g., Cl^-, H_2S). Omission of the related products of synproportionation is tantamount with confirmation (assumption) of the metastable state.

Another pitfall is involved with the precipitate formed. The term "precipitate" may concern salts, acids (e.g., H_2SiO_3, HL species for 8–hydroxyquinoline or dimethyldioxime), or moderately soluble species such as iodine ($\mathbf{I}_2$) in the system KIO_3+ HCl + H_2SeO_3 (+$HgCl_2$) titrated with $C_6H_8O_6$ (11, 12, 21); $\mathbf{I}_2$ appears there as the solid on defined stage of the titration— both in presence and in absence of $HgCl_2$. Generally, the simulating computer program should check the correctness of the formulation and take into account all possible changes in phase composition of the system in question.

The species differing in a quantity of water involved can be considered as identical species; e.g., $H_2BO_3^-$ ion is sometimes

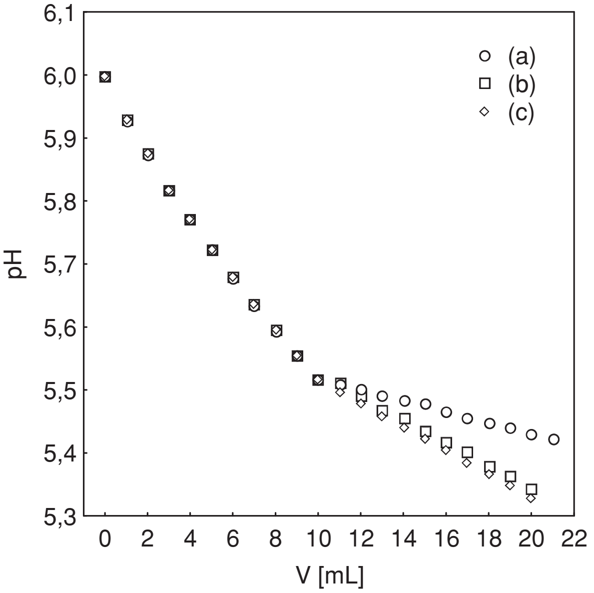

FIG. 2. The pH vs. V relationships plotted at $t_a = 15$ s and different $t = t_a + t_s$ assumed: (a) 20 s, (b) 90 s, and (c) 180 s; t_a—reagent addition period [s], t_s—stabilization period [s] (17).

written in the form $B(OH)_4^-$ or BO_2^-. The same remark concerns, e.g., the species: $H_4IO_6^-$ and IO_4^- or $Al(OH)_4^-$ and AlO_2^-.

ON THE COMPATIBILITY OF GEB—A COMPARATVE STUDY

One should ask whether the idea of GEB concept was unknown before 1992.

Chemists had an awareness of the necessity of completing the set of charge and concentration balances referred to as redox systems by an equation involving the species participating in redox (electron exchange) equilibria. For this purpose, the so-named "electron balances" (written in quotation marks and denoted later by an acronym EB), formed on the basis of redox notation, with coefficients resulting from stoichiometry of these reactions, resulting from experimental premises, were applied. It is evident, however, that the chemical reaction notation (the redox reaction, in particular) does not involve all the related species formed in the system in question.

As an example, one can quote EB formulated for the Fe(II) - MnO_4^- system considered above. The EB suggested was presented in the form

$$[Fe^{2+}] - 5[MnO_4^-] = (C_0V_0 - 5CV)/(V_0 + V) \qquad [86]$$

obtained on the basis of the reaction notation: $MnO_4^- + 5Fe^{2+} + 8H^+ = Mn^{2+} + 5Fe^{3+} + 4H_2O$. Note, however (Fig. 5), that concentrations of $MnSO_4$, Mn^{3+}, and $MnOH^{2+}$ species are comparable with $[Mn^{2+}]$ for $V > V_{eq}$.

Equation [86] should be put against full (and then correct) Eq. [48a]. In 1994, when the EB concept was still in common use, the GEB concept was termed as "electron prebalance," according to the suggestion of the editor of *Journal of Chemical Education*, where the first papers (9, 10) were issued.

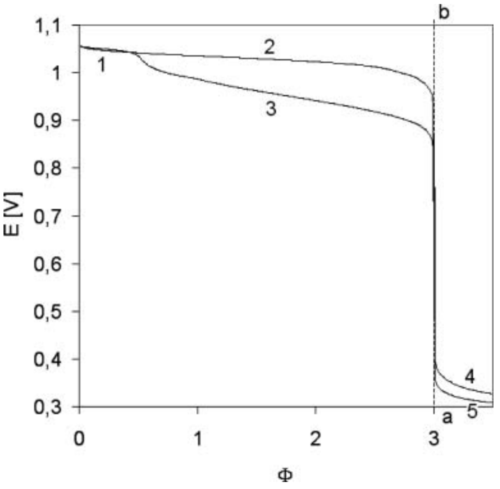

FIG. 3. The E vs. Φ relationships plotted under assumption that (i) $\beta = \gamma = 0$—curve 125; (*ii*) $\beta = 1$, $\gamma = 0$—curve 124; (*iii*) $\beta = 0$, $\gamma = 1$—curve 135; (*iv*) $\beta = \gamma = 1$—curve 134; $C_0 = 0.01$, $C_a = 0.02$, $C_{Se} = 0.02$, $C_{Hg} = 0.07$, $C = 0.1$ [mol/L], $\Phi = C{\cdot}V/(C_0{\cdot}V_0)$. For further details, see text.

Other balances, i.e., charge and concentration balances, can be formulated quite satisfactorily (completely), without any simplifications needed. Incomplete EB (e.g., one given by Eq. [86]), needs an incomplete form of the remaining balances, i.e., charge and concentration balances; otherwise, the system of contradictory equations is obtained. In order to avoid the consequences of this contradiction, one should apply one of the options:

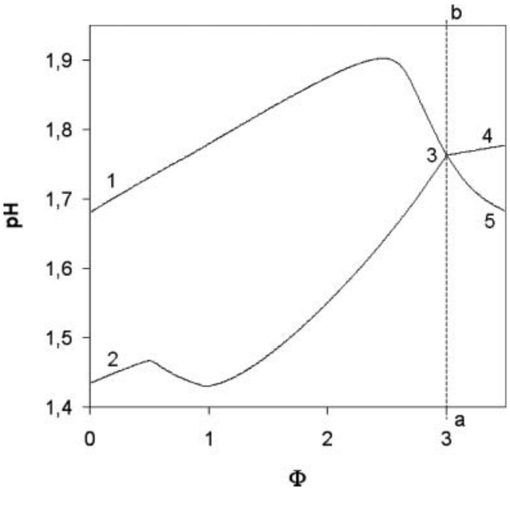

FIG. 4. The pH vs. Φ relationships plotted under assumption that (i) $\beta = \gamma = 0$—curve 134; (*ii*) $\beta = 1$, $\gamma = 0$—curve 135; (*iii*) $\beta = 0$, $\gamma = 1$—curve 234; (*iv*) $\beta = \gamma = 1$—curve 235; $C_0 = 0.01$, $C_a = 0.02$, $C_{Se} = 0.02$, $C_{Hg} = 0.07$, $C = 0.1$ [mol/L], $\Phi = C{\cdot}V/(C_0{\cdot}V_0)$. For further details, see text.

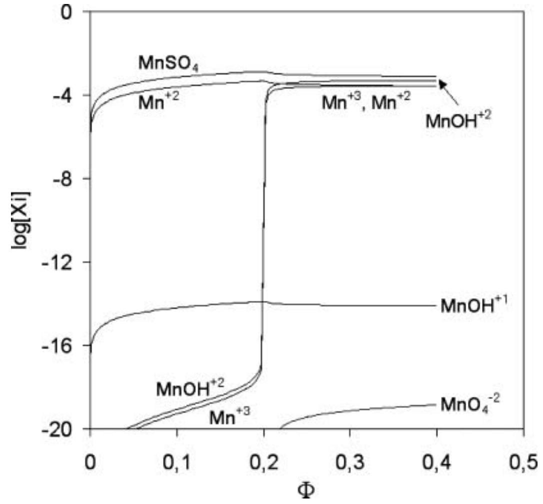

FIG. 5. The log[X_i] vs. Φ relationships for different manganese species X_i, plotted for titration of $V_0 = 100$ mL solution of $FeSO_4$ ($C_0 = 0.01$ mol/L) + H_2SO_4 ($C_a = 1.0$ mol/L) with V mL of C = 0.02 mol/L $KMnO_4$; $\Phi = C\cdot V/(C_0\cdot V_0)$. The species X_i are indicaed at the corresponding lines.

1° to complete EB with the lacking components (concentrations); this option can be realized within GEB, or

2° to impoverish the remaining balances to the level of ignorance represented by EB.

Because the option 2° appeared to be drastic and then unacceptable, as a rule, the approaches based on the Ringbom's stability constants concept (22) has been practiced, e.g., in (23), where some functional relationships were formulated and additional assumptions, such as constancy of pH-value during titration, were done. In effect, the considerations were limited only to buffered solutions. However, redox equilibria are referred also to the systems, where the simplifying assumption pH = const is invalid, in principle. It refers, e.g., to titration of Br_2 solution with NaOH (10). It should be noticed that the assumption pH = const makes the results distorted, also in buffered media, as were indicated in ref. (11), where the comparative analyses of both approaches were done.

Moreover, in EB the titration curve has been divided into two parts: before ($V < V_{eq}$) and after ($V \geq V_{eq}$) the equivalence point. The region of the jump on the titration curve, *nota bene* the most interesting from analytical viewpoint (24–26), was thus omitted in considerations. One should be stressed that the equation obtained on the basis of GEB concept for a given system is obligatory within the whole V-range covered by the related titration curve.

Summarizing, one can state that GEB is fully compatible with the remaining balances. Thanks to GEB, the GATES concept has been formulated [see (4) and references cited therein]. From the GATES viewpoint, the stoichiometry of a reaction, particularly redox reaction, is not a primary but the derivative concept.

CONCLUSIONS

The electron balance (GEB) concept, presented in the papers (9–11) issued in 1994, remained practically unnoticed in literature. It was obtained from the balance of electrons ascribed to element(s) participating in the electron transitions, with no relevance to the chemical reactions notation. Later on, this concept has been undertaken only by Macca (27) who tried to derive the balances known to him in (11) on the basis of strange manipulations done on the redox reactions notations. Macca's approach looks very artificial in context with the electron (pre)balance (GEB) formulation, and then it is not appropriate for wider application.

In this paper, the balances related to electrolytic systems are derived from fundamental, physical laws of conservation referred to electrolytic systems, separated from the environment by diathermal walls. On simple examples it is indicated, that the generalized electron balance (GEB) is simply the emanation of concentration balances for O and H, although its useful form can be obtained after linear combination of the resulting equation with charge and concentration balances. The general formula for GEB is derived for equilibrium and metastable systems. Apart from charge and concentration balances, GEB is one of the fundamental balances needed for mathematical description of redox systems.

The resolution of redox (and non–redox systems, as well) requires an application of more sophisticated, iterative computer programs. It particularly refers to pH–static titration, realized with use of two titrants, added alternately and repeatedly into a titrand (7, 8). The Gran (I, II) methods were previously considered as unacceptable for redox systems (28, 29). However, as indicated in our later paper (5) and references cited therein, some essential modifications done in the Gran methods provided the useful tools for determination of equivalence volume (V_{eq}) and true slope value of the redox indicator electrode applied in potentiometric redox titrations. In (30), only the species entering the reaction notation $Fe^{2+} + Ce^{4+} = Fe^{3+} + Ce^{3+}$ were considered in the related balances—despite the fact that strong sulphate complexes [e.g., $Fe(SO_4)_2^-$, $\log K_2 = 7.4$, or $Ce(SO_4)_2$, $\log K_2 = 10.4$] are formed in the system in question. *Nota bene*, the latter system was thoroughly considered in (11), in its "normal" titrimetric mode.

The thermodynamic approach based on material (charge, concentration, and electron) balances is a firm and valuable tool that enables the best *a priori* conditions of chemical analyses performed in electrolytic systems to be chosen. It is adaptable for equilibrium and metastable systems, where *quasistatic* isothermal processes take place. A special emphasis has been put on complex analytical systems where all (i.e., acid–base, redox, complexation, and precipitation) types of chemical reactions occur simultaneously and/or sequentially. All attainable physicochemical knowledge can be involved in calculations and no simplifying assumptions are needed.

The approach enables all possible (from thermodynamic viewpoint) reactions to be included and all effects resulting from the metastable state of the system and/or an incomplete set of equilibrium data presumed to be tested. It particularly refers to the $MnO_4^- + H_2O$ system where—taking the matter from thermodynamic viewpoint—water should be oxidized into O_2 in neutral media (11). Omission of the related products (e.g., O_2, H_2O_2, HO_2^-, MnO_2) in material balances is tantamount with acceptance of the metastable state of this system. The effect of presumable complexes of $Mn(SO_4)_i^{+3-2i}$ type and their strength (expressed by stability constants presumed) on the shape of titration curve has been considered (11).

Resolution of equilibria and titrations are justly considered among the most difficult topics of interest (31) although the reasons (accents) of these difficulties are not posed correctly. Namely, such limitations as a non–linearity of balances do not exist at all in the light of the possibilities offered by the iterative computer programs. Any analytical system is represented by a set of non–linear equations, after all. It should be also stressed that the approaches practiced until now are based on "electron balances" involving only the species entering the related reaction notation and the stoichiometry resulting from this notation (24) or, additionally, on application (23) of the Ringbom's idea of conditional equilibrium constants (22). Both approaches have nothing common with the GEB concept devised by Michałowski.

According to my experience, the main difficulties in the right description of redox systems arise on the line of junction between thermodynamics and kinetics; this line is not precisely defined in many metastable systems. One should notice that involving some species or a group of species in the balances is tantamount with "overthrowing" the potential barrier for a reaction that is effective from a thermodynamic viewpoint, but does not proceed with respect to the kinetics involved.

All the resulting inferences are based on firm, mathematical (algebraic) foundations, not on an extremely "fragile" chemical notation principle that is only a faint imitation of a true, algebraic notation. The new approach allows one to understand far better all physicochemical phenomena occurring in the system in question. Particularly, the application of the GEB concept enabled us to state a unique property: non-monotonicity of pH vs. V relationships (V—volume of titrant added) (8, 11, 12).

It is noteworthy that the knowledge of algebra requires—from a formal viewpoint—only the capabilities involved with an arrangement of the corresponding material balances and formulation of relationships based on the principle of mass action law.

Testing the complex redox and non–redox systems with the use of iterative computer programs deserves wider popularization among chemists and analysts. This way, some analytical procedures can be optimized and the best *a priori* conditions of analyses can be chosen. The results obtained from equilibrium (thermodynamic) simulated analysis can always be considered as a reference to the real behavior of the system tested, frequently corrupted by kinetic phenomena. It also enables one to demonstrate limitations of some analytical methods, e.g., ones concerning accuracy and precision of the pH–static titration (7, 8).

The GEB concept, referred to aqueous systems, results simply from elemental balances for oxygen (O) and hydrogen (H). The more comfortable form of GEB can be obtained from comparison with the related charge and elemental balances. The equation for GEB is the segment compatible with charge and concentration balances. This set of balances is needed for thermodynamic description of any (equilibrium or metastable) electrolytic (mono- or two-phase, static, or dynamic) system. It links four kinds of elementary (acid-base, redox, complexation, and precipitation) interactions met in electrolytic systems. In this respect, it has some resemblance to the (still unresolved) problem of Unified Field Theory, referred to four kinds of interactions known in physics. The approach can also be extended on liquid-liquid extraction systems and referred to gaseous mixtures, where redox reactions occur. In this paper, both static and dynamic (titration) redox systems will be considered.

FINAL COMMENTS

Mathematical character of phenomena belongs to the most exciting secrets of nature. The statement "All in World proceeds in mathematical manner", pronounced by G.W. Leibnitz (1646–1716), is still relevant, even in chemistry. When testing a phenomenon in physical or chemical systems, quantitatively, the principal challenge aims to establish a mathematical relationship between the variables tested. Such an approach may provide a better understanding of phenomena occurred in the system, in accordance with Kant's statement that "the knowledge contents equals to the mathematics involved."

An equation (or a set of equations) describing a system expresses the mathematical model of the system. Particularly, the electrolytic systems are described by algebraic equations (thermodynamic approach) or by a set of algebraic and differential equations (kinetic approach) (12). The model, based on correct and consistent preliminary assumptions, offers better understanding of the system tested. The inferences resulting from mathematical models may provide new conclusions, ideas, and expectations. What is more, some inferences can be formulated *a priori*, on the basis of simulating calculations, particularly ones referred to thermodynamic systems. When applying all attainable physicochemical data, it is possible to foresee and explain some phenomena on the basis of other phenomena. Among others, the best conditions of analysis (optimisation *a priori*) can be chosen. Another important advantage offered by the simulating procedures is the possibility to follow some details invisible in experiment; it particularly refers to dynamic speciation analysis, realized in simulated titrations. All the remarks are involved with chemometric approach to chemical systems. The chemometrics is perceived as a science related to chemical systems, with dynamic chemical processes included, via application of mathematical or statistical methods.

In mathematical modelling, with the simulation involved, elaborated nowadays with use of computer programming, the preliminary formulation of mathematical relations is necessary. The mathematical model, prepared for calculation as a computer program, should be defined through numerical values of the parameters involved. The (quantitative, in principle) results of calculations enable the qualitative conclusions to be drawn correctly. The mathematical relations, when interpreted, form a scientific theory. This relationship can be expressed in compact form as

$$\text{general algebra} + \text{logic} = \text{model theory}$$

Such a viewpoint was held by neo–positivists (physicists, mathematicians, and logicians) that have considered physics as the most exquisite science and aimed to unify the science on the physical mode, convincing that all other natural sciences, e.g., chemistry, biology, and psychology, should be considered from a physical viewpoint.

ABBREVIATIONS

C	concentration [mol/L] of a reagent in T
C_0	concentration [mol/L] of an analyte in D
D	titrand (solution titrated)
$\Phi =$	$CV/(C_0V_0)$ – fraction titrated
V	volume [mL] of T added
V_0	volume of D; T – titrant.

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