



Anna M Michałowska-Kaczmarczyk¹ and Tadeusz Michałowski^{2*}

¹Department of Oncology, The University Hospital in Cracow, 31-501 Cracow, Poland

²Faculty of Engineering and Chemical Technology, Technical University of Cracow, 31-155 Cracow, Poland

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***Corresponding author:** Tadeusz Michałowski, Faculty of Engineering and Chemical Technology, Technical University of Cracow, 31-155 Cracow, Poland, E-mail: michalot@o2.pl

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Review Article

The new paradigm in thermodynamic formulation of electrolytic systems – A review

Abstract

The general property of electrolytic systems in aqueous media is presented. The linear combination $f_{12} = 2 \cdot f(O) - f(H)$ of elemental balances: $f_1 = f(H)$ for $Y_1 = H$ and $f_2 = f(O)$ for $Y_2 = O$, is put in context with charge balance ($f_0 = ChB$) and other elemental and/or core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) related to the system in question. It is stated that f_{12} is (a) linearly independent on f_0, f_3, \dots, f_k for a redox system, or is (b) linearly dependent on f_0, f_3, \dots, f_k when related to a non-redox system. The balance $f_{12} = 2 \cdot f(O) - f(H)$ is the primary form of generalized electron balance (GEB), completing the set of equations needed for quantitative description of electrolytic redox systems, $f_{12} = pr$ -GEB. This manner of the GEB formulation needs none prior information on oxidation numbers for elements in components forming a (static or dynamic) redox system, and in the species of the system thus formed. The roles of oxidants and reductants are not indicated *a priori* at the stage of GEB formulation in redox systems. These properties can be generalized on non-redox and redox systems of any degree of complexity, also in mixed-solvent media, with amphiprotic co-solvent(s) involved. The article refers to simple (but unknown in earlier literature) regularities obligatory for electrolytic systems. All these regularities are exemplified by numerous examples of electrolytic systems, of different degree of complexity. The related systems are resolved with use of iterative computer programs, and illustrated graphically.

Abbreviations

D: Titrant; GATES: Generalized Approach to Electrolytic Systems; GEB: Generalized Electron Balance; GEM: Generalized Equivalent Mass; MAL: Mass Action Law; ON: Oxidation Number; T: Titrant; T: Temperature (K); V_0 : Volume [mL] of D; V: Volume [mL] of T.

Introduction

Any electrolytic system, can be perceived as a macroscopic part of the universe selected for observation and experimentation. For modeling purposes, the concept of a closed system:

matter \Leftrightarrow system/subsystems \Leftrightarrow heat

or its subsystems separated from the environment (surroundings) by diathermal (freely permeable by heat) walls as boundaries, is assumed in Generalized Approach to Electrolytic Systems (GATES) [1,2]. Diathermal walls are impermeable (\nleftrightarrow) to matter, but permeable (\Leftrightarrow) to heat. Thus the diathermal walls allow the heat exchange between the (sub) system(s), and the environment. The temperature changes, as

a result of exo- or endothermic effects occurring in the system, may influence the equilibrium constants values and, therefore, the system must be kept under isothermal conditions, ensured by diathermal walls during quasi-static, thermodynamic processes pre-assumed therein. Constant temperature ($T = \text{const}$) is one of the conditions securing constancy of equilibrium constants values during a titration. Any exchange of the matter (H_2O, CO_2, O_2, \dots) between the system and its environment is thus forbidden, for modeling purposes. Any chemical process, such as titration, with titrand D and titrant T as subsystems composing the D+T system, is carried out under isothermal conditions, in a *quasi-static* manner.

Within GATES, the elements conservation law relates to all components/species of the electrolytic system. The mass change involved with an (exo- or endothermal) effect is negligible (not measurable) when compared with total mass of the system. For example, the mass change, Δm , involved with enthalpy ΔH° of the reaction $H_{2(g)} + 0.5O_{2(g)} = H_2O_{(l)}$ ($\Delta H^\circ = -286 \text{ kJ/mol } H_2O$), equal $\Delta m = \Delta H^\circ/c^2 = -3.18 \cdot 10^{-9} \text{ g}$, is negligible when compared with 18 g of H_2O ; $c = 299792458 \text{ m/s}$ is the speed of light in vacuum. The neutralization or dilution give much smaller heat effects. The resulting law of mass preservation is then fulfilled,

irrespectively on whether stoichiometric or non-stoichiometric chemical reactions occur (or do not occur) in the system.

The quantitative, thermodynamic description of any electrolytic system requires prior information on: (1^o) the species present in the system considered; (2^o) the equilibrium constants; (3^o) the balances. The balances and expressions for equilibrium constants interrelate molar concentrations of some species in the system. To do it, we should necessarily define these terms in a unambiguous manner. This possibility is provided by the Generalized Approach to Electrolytic Systems (GATES) [1-39] which offers the best tool applicable for thermodynamic resolution of electrolytic systems, of any degree of complexity.

Laws of conservation – general remarks

The scientific laws are the statements used for description and prediction of some phenomena occurred in nature; they reflect causal relationships, fundamental to reality. Principally, all scientific laws follow from physics; laws in other sciences (chemistry, biology, ...) follow ultimately from physical laws. They were/are discovered and developed with use of mathematical tools, and supported by empirical evidence; mathematics is indispensable tool here. Scientific laws summarize and explain a large collection of facts determined by experiments. They are also able to predict the results of future experiments. The laws reflect scientific knowledge, repeatedly validated /verified (and never falsified) by experiments and observation. A law can usually be formulated as one or several algebraic equations, related to a closed system, that can be used to predict the outcome of an experiment, under given conditions of the processes taking place in a system.

Scientific theories are put in context with one or several laws, applied to express quantitatively the relationships between the variables measured in experiments, and explain qualitatively some properties of components present in the system tested. Creating the complete and compatible description of nature in the form of such laws is a fundamental aim of science [40].

Physical laws should be: 1. true, within their regime of validity; 2. simple, i.e., typically expressed in terms of mathematical equations; 3. universal, i.e., applicable everywhere; 4. progressive/groundbreaking, i.e., independent of the degree of complexity of the system, expressed by the number of variables characterizing the system. As an extra requirement put here is that they 5. should cover/include and explain other regularities known hitherto as rules, based on dubious preliminary assumptions. The oxidation number (ON) concept belongs to such rules.

All these general remarks/requirements, related to GATES and GATES/GEB in particular, are referenced to electrolytic systems (aqueous media), where the balances expressing the laws of charge and elements conservation in closed systems are formulated and interrelated in accordance with the principles of linear combination, known in elementary algebra. On this basis, the Generalized Electron Balance (GEB) concept, perceived as a Law of Nature, is derived from linear combination $f_{12} = 2f_2 - f_1$

of elemental balances: $f_1 = f(\text{H})$ for $Y_1 = \text{H}$ (hydrogen) and $f_2 = f(\text{O})$ for $Y_2 = \text{O}$ (oxygen). The linear combinations of f_{12} with charge $f_0 = \text{ChB}$ and other elemental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) of the system provide the criterion distinguishing between non-redox and redox systems, and formulation of the Generalized Electron Balance (GEB), perceived as a law of Nature, as the equation needed/indispensable for resolution of redox systems. The set of K independent balances $f_0, f_{12}, f_3, \dots, f_K$ is needed for balancing of a redox system, whereas $K-1$ balances f_0, f_3, \dots, f_K are needed for non-redox system. The multipliers applied purposely in linear combinations of the balances related to redox or non-redox systems provide the values of oxidation numbers (ON's) for elements of the system considered. The discussion on the linear independency/dependency property of the balances will be preceded by a simple example, known from elementary algebra.

Linear dependence of algebraic equations

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

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

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

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

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

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

Applying the matrix algebra, we see that the determinant

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

has zero value

$$D = c_1 \cdot \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{11} & a_{12} & a_{13} \end{vmatrix} + c_2 \cdot \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{21} & a_{22} & a_{23} \end{vmatrix} = c_1 \cdot 0 + c_2 \cdot 0 = 0$$

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

Checking the linear dependency or independency of linear algebraic equations is, in general case, a very burdensome and time-consuming task/activity, susceptible to simple mistakes, see comments in [32]. However, it turns out that the simple method of transformation of a linear combination of equations to the identity, $0 = 0$, is extremely effective, even in reference to complicated electrolytic systems. The rules involved with formulation of these combinations will be presented/exemplified in further sections of this paper.

Components and species

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

The terms: components of the system and species in the system are distinguished. After mixing the components, a mixture of defined species is formed. Thus the components form a (sub) system, and the species $X_i^{z_i} \cdot n_{iW}$ enter the system thus formed.

For some reasons, it is justifiable to start the balancing from the numbers of particular entities: N_{oj} – for components ($j = 1, \dots, J$) represented by molecules, and N_i – for species (ions and molecules) of i -th kind ($i = 1, \dots, I$), where I is the number of kinds of the species. The mono- or two-phase electrolytic system thus obtained involve N_1 molecules of H_2O and N_i species of i -th kind, $X_i^{z_i} \cdot n_{iW}$ ($i=2, 3, \dots, I$), specified briefly as $X_i^{z_i}$ (N_i, n_i), where $n_i \equiv n_{iW} \equiv n_i \text{H}_2\text{O}$. For ordering purposes, we write: H^+ (N_2, n_2), OH^- (N_3, n_3), \dots , i.e., $z_2 = 1, z_3 = -1, z_3 = -1, \dots$

The $X_i^{z_i}$'s with different numbers of H_2O molecules involved in $X_i^{z_i} \cdot n_{iW}$, e.g. H^+ , H_3O^+ and H_9O_4^+ ; H_4IO_6^- and IO_4^- , are considered equivalently, i.e., as the same species in this medium. The $n_i = n_{iW} = n_i \text{H}_2\text{O}$ values are virtually unknown – even for $X_2^{z_2} = \text{H}^+$ [41] in aqueous media, and depend on ionic strength (I) of the solution.

The notation $X_i^{z_i} \cdot n_{iW}$ for the species will be practiced on the step of formulation of the related balances. This viewpoint has several advantages. First, it presents the species in natural forms in aqueous media. This way, after linear combinations of the related balances, one can discover some regularities hidden earlier by notation of the species in the form $X_i^{z_i}$. This notation can be extended on electrolytic systems in mixed-solvent A_s ($s=1, \dots, S$) media, where mixed solvates $X_i^{z_i} n_{iA_1} \dots n_{iA_s}$ are assumed, and $n_{iA_s} \geq 0$ are the mean numbers of A_s ($s=1, \dots, S$) molecules attached to $X_i^{z_i}$ [33,34,42]. In other instances, the common/simpler notation $X_i^{z_i}$ of the species, e.g., $\text{HSO}_4^- \cdot n_5 \text{H}_2\text{O}$ as HSO_4^- , will be practiced. Molar concentrations [mol/L] of the species are denoted as $[X_i^{z_i}]$, for brevity. All concentrations of components and species be expressed in mol/L, and all volumes – in mL.

Notation of balances

In aqueous media, we formulate charge balance $f_0 = \text{ChB}$ and elemental balances: $f_1 = f(\text{H})$ for $E_1 = \text{H}$ (hydrogen) and $f_2 = f(\text{O})$ for $E_2 = \text{O}$ (oxygen), \dots . Other elemental or core balances will be denoted as $f_k = f(Y_k)$, $Y_k = E_k$ or *core_k* ($k=3, \dots, K$). A core is considered as a cluster of different atoms with defined composition (expressed by chemical formula), structure and external charge, unchanged in the system in question.

For example, SO_4^{-2} is a core within different sulfate species: $\text{HSO}_4^- \cdot n_4 \text{H}_2\text{O}$, $\text{SO}_4^{-2} \cdot n_5 \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot n_{11} \text{H}_2\text{O}$ in the D subsystem (I-2), considered in the System I.

In order to formulate the reliable (formally correct) balances for a given system, it is necessary to collect detailed, possibly complete (qualitative and quantitative) information regarding this system. The qualitative information concerns the components that make up the given system, and the species formed in this system. This information should subject thorough verification, for example regarding the preparation of the appropriate solutions; e.g. $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is dissolved in H_2SO_4 solution, not in pure, distilled water. The composition of chemical components is available in Internet. The collection of information about species formed in the system requires more effort. The source of information are here tables with appropriate physicochemical constants, such as dissociation constants of weak acids, stability constants of complexes, solubility products, etc. These constants interrelate concentrations of complex species with concentrations of their composing, simpler forms, involved in stoichiometric reaction, e.g. $\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{-2}$; $\text{Fe}^{+3} + 2\text{SO}_4^{-2} = \text{Fe}(\text{SO}_4)_2^{-1}$.

In quantitative description of redox systems, the standard potentials E_{oi} are also applied. The E_{oi} interrelate concentrations of the species with different oxidation degrees of a given element, involved in the related stoichiometric reaction, e.g., $\text{Fe}^{+3} + e^{-1} = \text{Fe}^{+2}$; $\text{MnO}_4^{-1} + 8\text{H}^{+1} + 5e^{-1} = \text{Mn}^{+2} + 4\text{H}_2\text{O}$. All the equilibrium constants were determined experimentally, and hence subjected to errors of various kind, as discussed e.g. in [32]. Nevertheless, despite these objections, the basic requirements must be met, namely: the set of these constants should be complete and consistent [27].

The components and species of redox systems are involved in GEB, charge (ChB), and concentration balances, and in a set of expressions for equilibrium constants. However, it should be taken into account that certain components (or groups of components) remain at metastable state with respect to each other, e.g. (1) KMnO_4 and H_2O [1], or (2) H_2S and H_2SO_4 [43], at room temperature. And so, KMnO_4 does not oxidize H_2O , and then none products of H_2O oxidation are formed in the system. Also none products of sulfur symproportionation are produced in the system formed from a mixture of diluted H_2S and H_2SO_4 solutions. On the other hand, in computer programs one can run some reaction paths to check “what would happen” if such reaction products were created in a metastable system (Figure 1). In these cases, one can compare the course/changes of the relevant measurands, e.g. pH and/or potential E , in a simulated titration procedure implemented in computer program, and in the experimental titration. In some cases, at the stage of collecting the relevant physicochemical data, one may have the impression of a lack of knowledge regarding the putative components in the respective systems. In any case, the putative components may be included in the respective balances, together with the corresponding equilibrium constants, pre-assumed arbitrarily. The dependences for measurable quantities obtained here can be then compared with the data obtained experimentally. On a similar principle,

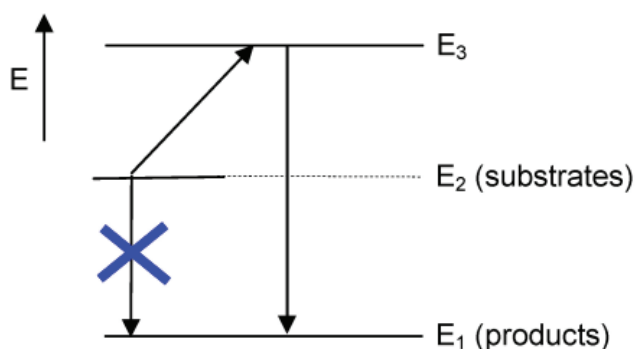


Figure 1: Graphical presentation of metastable state (level E2); spontaneous transition E2 → E1 is forbidden; E3–E2 = activation energy [1].

the simulated curves obtained after applying equilibrium data obtained from various sources (tables of equilibrium data) can be compared with each other, and with experimental results. On this simple way, one can get a lot of thermodynamic information about the system tested. Undoubtedly, this 'theme and variations' requires a kind of intellectual activity.

Titrand, titrant and titration

Static and dynamic systems, with water as the main component/solvent, are considered below. A static system is obtained by disposable mixing different components, as solutes, with water. In particular, titrant T and titrand D can be perceived as static subsystems of the dynamic D+T system, realized during the titration $T(V) \Rightarrow D(V_0)$, where – at defined point of the titration – V mL of T is added into V_0 mL of D and V_0+V mL of D+T system/mixture is thus obtained, if the assumption of additivity in the volumes is valid/tolerable. In general, D and T are composed of one or more solutes dissolved in water. In a computation procedure, V is considered as the steering variable.

Fraction titrated, titration curves

The results of simulated titrations, with measurable values: pH and/or potential E of D+T system registered, are plotted as functions of volume V of the titrant (T) added, i.e., $pH = pH(V)$, $E = E(V)$.

In some instances, it is advantageous/reasonable to plot the graphs: $E = E(\Phi)$ (e.g. Figure 5a), $pH = pH(\Phi)$ (Figure 5b), with the fraction titrated [1,4,7,8,44]

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \quad (1)$$

on the abscissa, where C_0 – concentration [mol/L] of analyte A in D, C – concentration [mol/L] of reagent B in T; it provides a kind of uniformity/normalization of the related plots.

Speciation graphs

The changes in concentrations of the species during a titration can be represented on speciation graphs as dynamic speciation curves, with $\log[X_i^{z_i}]$ on the ordinate and V or Φ on the abscissa (semi-logarithmic scale). Btw, the curves: $E = E(V)$, $pH = pH(V)$ and $E = E(\Phi)$, $pH = pH(\Phi)$ are also considered

as plots in semi-logarithmic scale. The samples with more components can be also considered on the related graphs, with the species grouped for clarity of presentation, see e.g. Figure 22.

In some instances, it is advisable to plot the static speciation curves, represented (in the logarithmic scale) by the $\log[X_i^{z_i}]$ vs. $\log C_0$ relationships. In context with the dynamic speciation curves, the static titration curves represent the effect of dilution of a sample with a component X (C_0) in pure water, see [12] (p. 529, X = Cl₂).

Charge and elemental/core balances – general notations

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

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

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

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

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

$$f_2 = f(O) = N_1 + \sum_{i=2}^I (a_{2i} + n_{i,w}) \cdot N_i - \sum_{j=1}^J b_{2j} \cdot N_{0j} = 0 \quad (4)$$

Then the balance

$$f_{12} = 2 \cdot f_2 - f_1 = \sum_{i=2}^I (2 \cdot a_{2i} - a_{1i}) \cdot N_i - \sum_{j=1}^J (2 \cdot b_{2j} - b_{1j}) \cdot N_{0j} = 0 \quad (5)$$

is formulated.

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

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

where a_{ki} and b_{kj} are the numbers of elements/cores Y_k in $X_i^{z_i} \cdot n_{i,w}$, and in the j-th component of the system, resp. For example, N_4 species $\text{HSO}_4^{-1} \cdot n_4 \text{H}_2\text{O}$ involve $N_4(1+2n_4)$ atoms of H (where $a_{12}=1$), $N_4(4+n_4)$ atoms of O (where $a_{22}=4$), and N_4 atoms of S; N_{05} molecules of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as a component involve $14N_{05}$ atoms of H, $11N_{05}$ atoms of O, N_{05} atoms of S and N_{05} atoms of Fe, i.e., $b_{15}=14$, $b_{25}=11$, $b_{35}=1$, $b_{55}=1$.

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

$0 = 0$. For a redox system, the proper linear combination of the balances gives the simplest/shortest form of GEB.

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

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

for elements with negative oxidation numbers, or

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

for elements with positive oxidation numbers, $k \in 3, \dots, K$. In this notation, f_k will be essentially treated not as the algebraic expression on the left side of the equation $f_k = 0$, but as an equation that can be expressed in alternative forms presented above.

The linear combination

$$f_0 + f_{12} - \sum_{k=3}^K d_k \cdot f_k = 0 \Leftrightarrow \sum_{k=3}^K d_k \cdot f_k - f_{12} - f_0 = 0 \Leftrightarrow \quad (7)$$

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

involves K balances: $f_0, f_{12}, f_3, \dots, f_K$. In particular, $d_1 = +1$, $d_2 = -2$. As will be indicated below, the multipliers d_k are equal to (or involved with) the oxidation numbers (ON's) of the corresponding elements E_k , $Y_k = E_k$ ($k \in 1, \dots, K$). It enables to get the simplest (most desired) form of the related linear combination (Eq. 7), as will be explained in examples presented below.

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

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

The elemental/core balances, expressed in terms of particular units: N_{0j} for components and N_i for species, are the basis to formulation of Generalized Electron Balance (GEB), charge balance (ChB) and concentration balances, expressed in terms of molar concentrations.

Some computational details

We deal here with the set of non-linear algebraic equations, solvable by means of iterative computer programs. In principle, any iterative computer program can be used for this purpose. The titrations presented here were simulated using an iterative computer program (MATLAB software [1,45], included in the Optimization Toolbox™); other examples are presented e.g. in [14,15,22,25]. Some examples of computer programs are also

outlined in this chapter. The properly formulated balances describing the titration process can be generally written as a set of equations: $F_k = F_k(\mathbf{x}) = 0$, where $\mathbf{x} = \mathbf{x}(V) = [x_1, \dots, x_k, \dots, x_K]^T$ is the vector of basic variables $x_k = x_k(V)$ ($k = 1, \dots, K$). For each V value, the corresponding sum of squares is minimized $SS = SS(V) = \sum_{k=1}^K [F_k(\mathbf{x}(V))]^2$, i.e., $SS(V) \rightarrow 0$ for all V values taken from a pre-assumed V -interval.

Some points (V_j, E_j) from the jump region are obtained by performing subsequent iterations at reduced steps, $V_{j+1} - V_j$, corresponding to subsequent titrant additions, see e.g. the data specified in Tables 2,3.

All these activities and the resulting properties will be confirmed in the examples specified below.

Specification of the systems tested

The principal ideas of GATES/GEB will be exemplified in redox systems I – VI, specified in Table 1. After formulation of the related balances, the results obtained from calculations, made according to iterative computer programs, will be presented graphically, and in the related tables. The results will be considered from the Generalized Equivalent Mass (GEM) viewpoint [4,8]. The original methods of equivalence volume (V_{eq}) determination will be applied for the systems I and II, and completed by the analysis made in the system VI (Table 1).

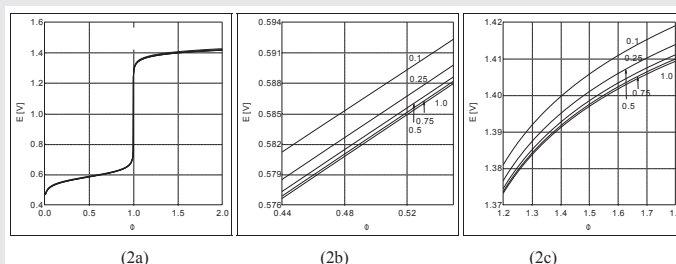


Figure 2: System I-3: (2a) The $E = E(\phi)$ curves plotted for the D+T system, at $V_0 = 100$, $C_0 = 0.01$, $C = 0.1$, $C_1 = 0.5$ and different C_{01} values, indicated at their enlarged fragments: (2b) at $\phi < \phi_{eq}$, (2c) at $\phi > \phi_{eq}$.

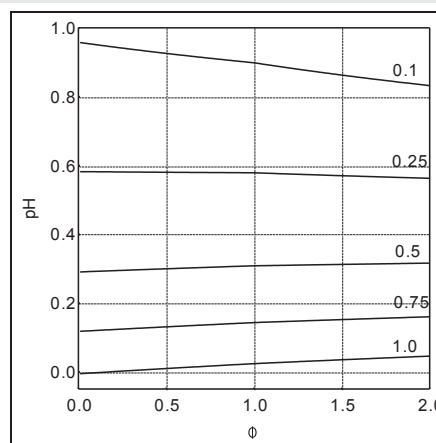


Figure 3: System I-3: The $pH = pH(\phi)$ relationship for the D+T system at $V_0 = 100$, $C_0 = 0.01$, $C = 0.1$, $C_1 = 0.5$ and different C_{01} values indicated at the corresponding lines.

Table 1: Specification of the redox systems considered herein.

No.	T (V)	D (V ₀)
I-3	Ce(SO ₄) ₂ (C) + H ₂ SO ₄ (C ₁) + CO ₂ (C ₂)	FeSO ₄ (C ₀) + H ₂ SO ₄ (C ₀₁) + CO ₂ (C ₀₂)
II-3	KMnO ₄ (C) + CO ₂ (C ₁)	FeSO ₄ (C ₀) + H ₂ SO ₄ (C ₀₁) + CO ₂ (C ₀₂)
III-3	KMnO ₄ (C) + CO ₂ (C ₁)	FeSO ₄ (C ₀₁) + H ₂ C ₂ O ₄ (C ₀₂) + H ₂ SO ₄ (C ₀₃) + CO ₂ (C ₀₄)
III-3a	KMnO ₄ (C) + CO ₂ (C ₁)	H ₂ C ₂ O ₄ (C ₀₂) + H ₂ SO ₄ (C ₀₃) + CO ₂ (C ₀₄)
IV	K ₂ Cr ₂ O ₇ (C)	KI (C ₀) + H ₂ SO ₄ (C ₀₁)
V	NH ₃ (C ₁), CH ₃ COOH (C ₂), KI (C ₃), Na ₂ S ₂ O ₃ (C)	CuSO ₄ (C ₀) + H ₂ SO ₄ (C ₀₁)
VI	KMnO ₄ (C)	FeSO ₄ (C ₀₂) + Fe(SO ₄) ₃ (C ₀₃) + H ₂ SO ₄ (C ₀₄)

System I

We consider here non-redox subsystems:

(I-1) T (V) subsystem, composed of Ce(SO₄)₂·4H₂O (N₀₁) + H₂SO₄ (N₀₂) + H₂O (N₀₃) + CO₂ (N₀₄);

(I-2) D (V₀) subsystem, composed of FeSO₄·7H₂O (N₀₅) + H₂SO₄ (N₀₆) + H₂O (N₀₇) + CO₂ (N₀₈);

and

(I-3) D+T (V₀+V) redox system, as the mixture of D and T, where the following species are formed:

H₂O (N₁); H⁺ (N₂, n₂), OH⁻ (N₃, n₃), HSO₄⁻ (N₄, n₄), SO₄⁻² (N₅, n₅), H₂CO₃ (N₆, n₆), HCO₃⁻ (N₇, n₇),

CO₃⁻² (N₈, n₈), Fe⁺² (N₉, n₉), FeOH⁺¹ (N₁₀, n₁₀), FeSO₄ (N₁₁, n₁₁), Fe⁺³ (N₁₂, n₁₂), FeOH⁺² (N₁₃, n₁₃),

Fe(OH)₂⁺¹ (N₁₄, n₁₄), Fe₂(OH)₂⁺⁴ (N₁₅, n₁₅); FeSO₄⁺¹ (N₁₆, n₁₆), Fe(SO₄)₂⁻¹ (N₁₇, n₁₇), Ce⁺⁴ (N₁₈, n₁₈),

CeOH⁺³ (N₁₉, n₁₉), Ce₂(OH)₃⁺⁵ (N₂₀, n₂₀), Ce₂(OH)₄⁺⁴ (N₂₁, n₂₁), CeSO₄⁺² (N₂₂, n₂₂), Ce(SO₄)₂ (N₂₃, n₂₃), Ce(SO₄)₃⁻² (N₂₄, n₂₄), Ce⁺³ (N₂₅, n₂₅), CeOH⁺² (N₂₆, n₂₆), CeSO₄⁺¹ (N₂₇, n₂₇), Ce(SO₄)₂⁻¹ (N₂₈, n₂₈),

Ce(SO₄)₃⁻³ (N₂₉, n₂₉) (8)

For example, the notation HSO₄⁻¹ (N₄, n₄) applied there refers to N₄ ions of HSO₄⁻¹·n₄H₂O involving: N₄(1+2n₄) atoms of H, N₄(4+n₄) atoms of O, and N₄ atoms of S.

The presence of CO₂ in T and D is considered here as an admixture from air, to imitate real conditions of the analysis, on the step of preparation of D and T; the titration T(V) ⇒ D(V₀) is realized in the closed system, under isothermal conditions. The D+T dynamic redox system is then composed of non-redox static subsystems: D and T. On this basis, some general properties involved with non-redox and redox systems will be indicated. Different forms of GEB, resulting from linear combinations of charge and elemental balances related to D+T system, will be obtained. To avoid (possible) disturbances, the common notation (subscripts) assumed in the set (8) of species will be applied for components and species in T, D and D+T. In context with the dynamic D+T system, T and D are considered as static (sub)systems.

Linear combination of balances

The T subsystem (I-1):

We get here the balances:

$$f_0 = \text{ChB}$$

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

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

$$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_{18}n_{18} +$$

$$N_{19}(1+2n_{19}) + N_{20}(3+2n_{20}) + N_{21}(4+2n_{21}) + 2N_{22}n_{22} + 2N_{23}n_{23} + 2N_{24}n_{24} = 8N_{01} + 2N_{02} + 2N_{03}$$

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

$$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_{18}n_{18} +$$

$$N_{19}(1+n_{19}) + N_{20}(3+n_{20}) + N_{21}(4+n_{21}) + N_{22}(4+n_{22}) + N_{23}(8+n_{23}) + N_{24}(12+n_{24})$$

$$= 12N_{01} + 4N_{02} + N_{03} + 2N_{04}$$

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

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

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

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

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

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

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

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

$$= 16N_{01} + 6N_{02} + 4N_{04}$$

The linear combination

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

as the simple sum of collected balances:

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

$$= 16N_{01} + 6N_{02} + 4N_{04}$$

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

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

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

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

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

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

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

The D subsystem (I-2):

We get here the balances:

$$f_0 = \text{ChB}$$

$$N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 2N_9 + N_{10} = 0 \quad (11)$$

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

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

$$N_{10}(1+2n_{10}) + 2N_{11}n_{11} = 14N_{05} + 2N_{06} + 2N_{07}$$

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

$$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_9n_9 +$$

$$N_{10}(1+n_{10}) + N_{11}(4+n_{11}) = 11N_{05} + 4N_{06} + N_{07} + 2N_{08}$$

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

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

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

$$N_{08} = N_6 + N_7 + N_8 \quad (12)$$

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

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

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

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

The linear combination

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

as the simple sum of collected balances:

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

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

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

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

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

is transformed into identity, $0 = 0$.

The balance (13) can be rewritten into equivalent forms

$$2 \cdot f_2 - f_1 + f_0 - 6 \cdot f_3 - 4 \cdot f_4 - 2 \cdot f_5 = 0 \quad | \cdot (-1) \Leftrightarrow (+1) \cdot f_1 + (-2) \cdot f_2 + (+6) \cdot f_3 + (+4) \cdot f_4 + (+2) \cdot f_5 - f_0 = 0 \Leftrightarrow (+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+6) \cdot f(\text{SO}_4) + (+4) \cdot f(\text{CO}_3) + (+2) \cdot f(\text{Fe}) - \text{ChB} = 0 \quad (14)$$

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

The D+T system (I-3):

For the D+T system we have the balances:

$$f_0 = \text{ChB}$$

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

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

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

$$2N_{29}n_{29} = 8N_{01} + 2N_{02} + 2N_{03} + 14N_{05} + 2N_{06} + 2N_{07}$$

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

$$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_9n_9 +$$

$$N_{10}(1+n_{10}) + N_{11}(4+n_{11}) + N_{12}n_{12} + N_{13}(1+n_{13}) + N_{14}(2+n_{14}) + N_{15}(2+n_{15}) + N_{16}(4+n_{16}) + N_{17}(8+n_{17}) + N_{18}n_{18} + N_{19}(1+n_{19}) + N_{20}(3+n_{20}) + N_{21}(4+n_{21}) + N_{22}(4+n_{22}) + N_{23}(8+n_{23}) + N_{24}(12+n_{24}) + N_{25}n_{25} + N_{26}(1+n_{26}) + N_{27}(4+n_{27}) + N_{28}(8+n_{28}) + N_{29}(12+n_{29}) = 12N_{01} + 4N_{02} + N_{03} + 2N_{04} + 11N_{05} + 4N_{06} + N_{07} + 2N_{08}$$

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

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

$$2N_{28} + 3N_{29} \quad (16)$$

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

$$N_{04} + N_{08} = N_6 + N_7 + N_8 \quad (17)$$

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

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

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

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

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

$$-N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} + N_{13} +$$

$$2N_{14} + 2N_{15} + 8N_{16} + 16N_{17} + N_{19} + 3N_{20} + 4N_{21} + 8N_{22} + 16N_{23} + 24N_{24} + N_{26} + 8N_{27} + 16N_{28} + 24N_{29} = 16N_{01} + 6N_{02} + 4N_{04} + 8N_{05} + 6N_{06} + 4N_{08} \quad (20)$$

The linear combination

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

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

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

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

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

$$12N_{01} + 6N_{02} + 6N_{05} + 6N_{06} = 6N_4 + 6N_5 + 6N_{11} + 6N_{16} + 12N_{17} + 6N_{22} + 12N_{23} + 18N_{24} + 6N_{27} + 12N_{28} + 18N_{29}$$

$$4N_{04} + 4N_{08} = 4N_6 + 4N_7 + 4N_8$$

It gives the equation

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

Denoting atomic numbers: $Z_{\text{Fe}} = 26$, $Z_{\text{Ce}} = 58$, from Equations: 18, 19 and 22, we obtain the balance

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

Applying the relations:

$$[x_1^{z_1}] \cdot (V_0 + V) = 10^3 \cdot \frac{N_1}{N_A}, C_0 V_0 = 10^3 \cdot N_{01} / N_A, \text{ and } CV = 10^3 \cdot N_{05} / N_A \quad (24)$$

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

$$\begin{aligned} & (Z_{\text{Fe}} - 2)([\text{Fe}^{+2}] + [\text{FeOH}^{+1}] + [\text{FeSO}_4]) + (Z_{\text{Fe}} - 3)([\text{Fe}^{+3}] + \\ & [\text{FeOH}^{+2}] + [\text{Fe}(\text{OH})_2^{+1}] + 2[\text{Fe}_2(\text{OH})_2^{+4}] \\ & + [\text{FeSO}_4^{+1}] + [\text{Fe}(\text{SO}_4)_2^{-1}] + (Z_{\text{Ce}} - 4)([\text{Ce}^{+4}] + [\text{CeOH}^{+3}] + \\ & 2[\text{Ce}_2(\text{OH})_3^{+5}] + 2[\text{Ce}_2(\text{OH})_4^{+4}] + [\text{CeSO}_4^{+2}] + [\text{Ce}(\text{SO}_4)_2] + \\ & [\text{Ce}(\text{SO}_4)_3^{-2}] + (Z_{\text{Ce}} - 3)([\text{Ce}^{+3}] + [\text{CeOH}^{+2}] + [\text{CeSO}_4^{+1}] + \\ & [\text{Ce}(\text{SO}_4)_2^{-1}] + [\text{Ce}(\text{SO}_4)_3^{-3}]) \end{aligned}$$

$$= ((Z_{\text{Fe}} - 2) \cdot C_0 V_0 + (Z_{\text{Ce}} - 4) \cdot CV) / (V_0 + V) \quad (23a)$$

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

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

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

$$[\text{Fe}^{+2}] + [\text{FeOH}^{+1}] + [\text{FeSO}_4] - ([\text{Ce}^{+4}] + [\text{CeOH}^{+3}] + 2[\text{Ce}_2(\text{OH})_3^{+5}] + 2[\text{Ce}_2(\text{OH})_4^{+4}] +$$

$$[\text{CeSO}_4^{+2}] + [\text{Ce}(\text{SO}_4)_2] + [\text{Ce}(\text{SO}_4)_3^{-2}]) = (C_0 V_0 - CV) / (V_0 + V) \quad (25a)$$

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

$$-[\text{H}^{+1}] + [\text{OH}^{-1}] + 7[\text{HSO}_4^{-1}] + 8[\text{SO}_4^{-2}] + 4[\text{H}_2\text{CO}_3] + 5[\text{HCO}_3^{-1}] + 6[\text{CO}_3^{-2}] + [\text{FeOH}^{+1}] + 8[\text{FeSO}_4] +$$

$$[\text{FeOH}^{+2}] + 2[\text{Fe}(\text{OH})_2^{+1}] + 2[\text{Fe}_2(\text{OH})_2^{+4}] + 8[\text{FeSO}_4^{+1}] + 16[\text{Fe}(\text{SO}_4)_2^{-1}] + [\text{CeOH}^{+3}] + 3[\text{Ce}_2(\text{OH})_3^{+5}] + 4[\text{Ce}_2(\text{OH})_4^{+4}] + 8[\text{CeSO}_4^{+2}] + 16[\text{Ce}(\text{SO}_4)_2] + 24[\text{Ce}(\text{SO}_4)_3^{-2}] + [\text{CeOH}^{+2}] + 8[\text{CeSO}_4^{+1}] + 16[\text{Ce}(\text{SO}_4)_2^{-1}] + 24[\text{Ce}(\text{SO}_4)_3^{-3}] = (16CV + 6(C_0 V_0 + C_1 V) + 4(C_0 V_0 + C_2 V)) / (V_0 + V) \quad (20a)$$

where, in addition to relations 24, we apply $C_1 V = 10^3 \cdot \frac{N_{02}}{N_A}$, $C_0 V_0 = 10^3 \cdot \frac{N_{06}}{N_A}$, $C_2 V = 10^3 \cdot \frac{N_{04}}{N_A}$, $C_0 V_0 = 10^3 \cdot \frac{N_{08}}{N_A}$ (26)

From Eq. 22 we have

$$2 \cdot ([\text{Fe}^{+2}] + [\text{FeOH}^{+1}] + [\text{FeSO}_4]) + 3 \cdot ([\text{Fe}^{+3}] + [\text{FeOH}^{+2}] + [\text{Fe}(\text{OH})_2^{+1}] + 2[\text{Fe}_2(\text{OH})_2^{+4}] +$$

$$[\text{FeSO}_4^{+1}] + [\text{Fe}(\text{SO}_4)_2^{-1}] + 4 \cdot ([\text{Ce}^{+4}] + [\text{CeOH}^{+3}] + 2[\text{Ce}_2(\text{OH})_3^{+5}] + 2[\text{Ce}_2(\text{OH})_4^{+4}] + [\text{CeSO}_4^{+2}] +$$

$$[\text{Ce}(\text{SO}_4)_2] + [\text{Ce}(\text{SO}_4)_3^{-2}]) + 3 \cdot ([\text{Ce}^{+3}] + [\text{CeOH}^{+2}] + [\text{CeSO}_4^{+1}] + [\text{Ce}(\text{SO}_4)_2^{-1}] + [\text{Ce}(\text{SO}_4)_3^{-3}])$$

$$= (2 \cdot C_0 V_0 + 4 \cdot CV) / (V_0 + V) \quad (22a)$$

As we see, the linear combination $f_{12} + f_0 - 6f_3 - 4f_4 = 0$ of balances for electron-non-active elements and $f_0 = \text{ChB}$, gives the Equations 22a and 23a, containing only the components and species where electron-active elements (here: Fe, Ce) are involved. The coefficients/multipliers at the concentrations in Eq. 22a are equal to oxidation numbers of the corresponding components and species, with the electron-active elements involved.

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

$$[\text{Fe}^{+3}] + [\text{FeOH}^{+2}] + [\text{Fe}(\text{OH})_2^{+1}] + 2[\text{Fe}_2(\text{OH})_2^{+4}] + [\text{FeSO}_4^{+1}] + [\text{Fe}(\text{SO}_4)_2^{-1}] -$$

$$([\text{Ce}^{+3}] + [\text{CeOH}^{+2}] + [\text{CeSO}_4^{+1}] + [\text{Ce}(\text{SO}_4)_2^{-1}] + [\text{Ce}(\text{SO}_4)_3^{-3}]) = 0 \quad (27)$$

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

Equations 20a, 22a, 23a, 25a and 27, are equivalent to each other. All of them have full properties of the GEB, obtained according to Approach II to GEB, discussed widely in [1,3,5] and in some references cited therein. Other linear combinations of the balance f_{12} with f_0, f_3, \dots, f_6 are also acceptable/possible, from algebraic viewpoint. In particular, Eq. 19a is identical with the one obtained according to Approach I to GEB, obtained according to "card game" principle, described convincingly and illustrated artfully in [3] (pp. 41-43).

Briefly, according to Approach I to GEB, the common pool of electrons, introduced by Fe and Ce as the electron-active elements as 'players' [3], is $(Z_{Fe}-2) \cdot N_{01} + (Z_{Ce}-4) \cdot N_{05}$. These electrons are dissipated between different species formed by Fe and Ce in the mixture, namely: $(Z_{Fe}-2)N_9$ of Fe-electrons in $Fe^{+2} \cdot n_9 \cdot H_2O$, $(Z_{Fe}-2)N_{13}$ of Fe-electrons in $FeOH^{+1} \cdot n_{13} \cdot H_2O$, ... , $(Z_{Ce}-4)N_{18}$ of Ce-electrons in $Ce^{+4} \cdot n_{18} \cdot H_2O$, ... , $2(Z_{Ce}-4)N_{20}$ of Ce-electrons in $Ce_2(OH)_3^{+5} \cdot n_{20} \cdot H_2O$, ... , $(Z_{Ce}-3)N_{29}$ of Ce-electrons in $Ce(SO_4)_3^{-3} \cdot n_{29} \cdot H_2O$. Then the electron balance is presented by Eq. 21. This way, the equivalency of Approaches I and II to GEB is proved.

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

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

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

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

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

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

$$3[Ce(SO_4)_3^{-2}] + [CeSO_4^{+1}] + 2[Ce(SO_4)_2^{-1}] + 3[Ce(SO_4)_3^{-3}] -$$

$$(C_0V_0 + C_{01}V_0 + 2CV + C_1V)/(V_0+V) = 0 \quad (16a)$$

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

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

$$2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] +$$

$$[Fe(SO_4)_2^{-1}] - C_0V_0/(V_0+V) = 0 \quad (18a)$$

$$[Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}] +$$

$$[Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}] -$$

$$CV/(C_0+V) = 0 \quad (19a)$$

Independent equilibrium constants for this system are involved in relations:

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

$$[HCO_3^{-1}] = 10^{10.1}[H^{+1}][CO_3^{2-}]; [Fe^{+3}] = [Fe^{+2}] \cdot 10^{A(E - 0.771)}; [Ce^{+4}] = [Ce^{+3}] \cdot 10^{A(E - 1.70)};$$

$$[FeOH^{+1}] = 10^{4.5}[Fe^{+2}][OH^{-1}]; [FeOH^{+2}] = 10^{11.0}[Fe^{+3}][OH^{-1}]; [Fe(OH)_2^{+1}] = 10^{21.7}[Fe^{+3}][OH^{-1}]^2;$$

$$[Fe_2(OH)_2^{+4}] = 10^{21.7}[Fe^{+3}]^2[OH^{-1}]^2; [FeSO_4] = 10^{2.3}[Fe^{+2}][SO_4^{-2}]; [FeSO_4^{+1}] = 10^{4.18}[Fe^{+3}][SO_4^{-2}];$$

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

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

$$10^{53.7}[Ce^{+4}]^2[OH^{-1}]^4; [CeSO_4^{+1}] = 10^{1.63}[Ce^{+3}][SO_4^{-2}];$$

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

$$10^{3.08}[Ce^{+3}][SO_4^{-2}]^3; [CeSO_4^{+2}] = 10^{3.5}[Ce^{+4}][SO_4^{-2}];$$

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

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

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

$$\mathbf{x} = [x_1, \dots, x_6]^T = [E, pH, pCe_3, pFe_2, pSO_4, pH_2CO_3] \quad (29)$$

Potential E , $pH = -\log[H^{+1}]$, $pCe_3 = -\log[Ce^{+3}]$, $pFe_2 = -\log[Fe^{+2}]$, $pSO_4 = -\log[SO_4^{-2}]$,

$pH_2CO_3 = -\log[H_2CO_3]$ are defined for particular V values of the titrant added.

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

$$\left[e^{-1} \right] = 10^{-A \cdot E}, [H^{+1}] = 10^{-pH}, [Ce^{+3}] = 10^{-pCe_3}, [Fe^{+2}] = 10^{-pFe_2}, [SO_4^{-2}] = 10^{-pSO_4}, [H_2CO_3] = 10^{-pH_2CO_3} \quad (30)$$

where

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

Graphical presentation of results and discussion

The results of calculations realized for D+T system with use of MATLAB are presented in Figures 2-4 [39]. Figure 2a shows the redox titration curves $E = E(\Phi)$ in the D+T system, at different concentrations C_{01} of H_2SO_4 contained in the titrand (D). Some fragments of the curves, related to $\Phi < \Phi_{eq}$ and $\Phi > \Phi_{eq}$ are presented in extended scale in Figures 2b,c. The jump on the curve occurs at $\Phi = \Phi_{eq} = 1$, i.e., at the equivalent point where $C \cdot V_{eq} = C_0 \cdot V_0$. Points (V_j, E_j) in the jump region were obtained by performing subsequent iterations at a reduced

steps, $V_{j+1} - V_j$, corresponding to subsequent titrant additions.

Figure 3 shows the $\text{pH} = \text{pH}(\Phi)$ functions obtained under the same conditions (C_0, C_{01}, C, C_1), at which the curves in Figure 2 were plotted. The curves $\text{pH} = \text{pH}(\Phi)$ do not show any visible bend in the vicinity of $\Phi = \Phi_{\text{eq}} = 1$. It can be explained as the consequence of high buffer capacity of the solution [17], resulting from the presence of strong acid (H_2SO_4), with total concentration $(C_{01}V_0 + C_1V)/(V_0 + V)$. The direction of changes in the course of the respective curves in Figure 3 results from the difference between concentrations C_{01} (in D) and C_1 in T; at $C_1 < C_{01}$, the diluting effect from the titrant side is marked, which results in a small (relative) decrease of pH value.

Figure 4a,b shows speciation graphs for Fe and Ce species in the system. All the species involved in concentration balances for Fe (Eq. 18a) and Ce (Eq. 19a), are presented there. In particular, $[\text{Fe}^{+3}] \ll [\text{Fe}(\text{SO}_4)_2^{-1}]$, $[\text{Ce}^{+4}] \ll [\text{Ce}(\text{SO}_4)_3^{-2}]$, $[\text{Fe}^{+2}] < [\text{FeSO}_4]$ and $[\text{Ce}^{+3}] \approx [\text{CeSO}_4^{+1}]$, i.e., simple ions: Ce^{+4} , Fe^{+3} , Fe^{+2}

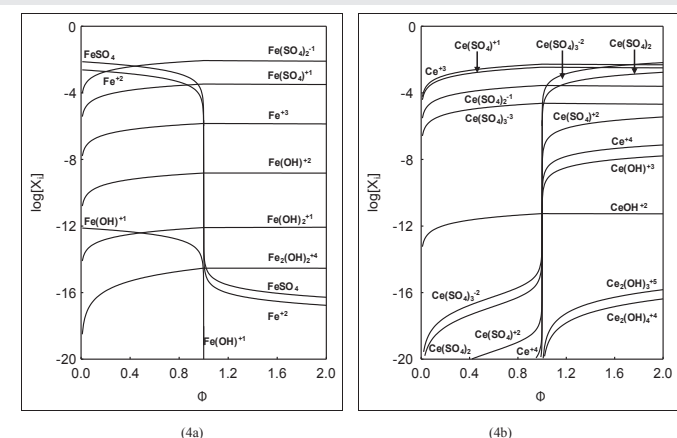


Figure 4: System I-3: Dynamic speciation curves plotted for (4a) Fe-species and (4b) Ce-species for the D+T system in Example 1, where $V_0 = 100$, $C_0 = 0.01$, $C_{01} = 1.0$, $C = 0.1$, $C_1 = 0.5$.

and Ce^{+3} are not predominant species in the system, also in the vicinity of $\Phi_{\text{eq}} = 1$.

System II

We consider here non-redox subsystems:

(II-1) T (V) subsystem, composed of KMnO_4 (N_{01}) + H_2O (N_{03}) + CO_2 (N_{04});

(II-2) D (V_0) subsystem, composed of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (N_{05}) + H_2SO_4 (N_{06}) + H_2O (N_{07}) + CO_2 (N_{08});

and

(II-3) D+T ($V_0 + V$) redox system, as the mixture of D and T, where the following species are formed:

H_2O (N_1); H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3), HSO_4^{-1} (N_4, n_4), SO_4^{-2} (N_5, n_5), H_2CO_3 (N_6, n_6), HCO_3^{-1} (N_7, n_7),

CO_3^{-2} (N_8, n_8), Fe^{+2} (N_9, n_9), FeOH^{+1} (N_{10}, n_{10}), FeSO_4 (N_{11}, n_{11}),

Fe^{+3} (N_{12}, n_{12}), FeOH^{+2} (N_{13}, n_{13}),

$\text{Fe}(\text{OH})_2^{+1}$ (N_{14}, n_{14}), $\text{Fe}_2(\text{OH})_2^{+4}$ (N_{15}, n_{15}); FeSO_4^{+1} (N_{16}, n_{16}), $\text{Fe}(\text{SO}_4)_2^{-1}$ (N_{17}, n_{17}), K^{+1} (N_{18}, n_{18}),

MnO_4^{-1} (N_{19}, n_{19}), MnO_4^{-2} (N_{20}, n_{20}), Mn^{+3} (N_{21}, n_{21}), MnOH^{+2} (N_{22}, n_{22}), Mn^{+2} (N_{23}, n_{23}), MnOH^{+1} (N_{24}, n_{24}), MnSO_4 (N_{25}, n_{25}) (31)

Precipitation of MnO_2 does not occur at sufficiently low pH value.

The complete set of equilibrium constants related to this D+T system is involved in the relations:

$$[\text{H}^{+1}][\text{OH}^{-1}] = 10^{-14.0}; [\text{HSO}_4^{-1}] = 10^{1.8}[\text{H}^{+1}][\text{SO}_4^{-2}]; [\text{H}_2\text{CO}_3] = 10^{16.4}[\text{H}^{+1}]^2[\text{CO}_3^{-2}]; [\text{HCO}_3^{-1}] = 10^{10.1}[\text{H}^{+1}][\text{CO}_3^{-2}]; [\text{Fe}^{+3}] =$$

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

$$= 10^{11.0}[\text{Fe}^{+3}][\text{OH}^{-1}]; [\text{Fe}(\text{OH})_2^{+1}] = 10^{21.7}[\text{Fe}^{+3}][\text{OH}^{-1}]^2; [\text{Fe}_2(\text{OH})_2^{+4}] = 10^{21.7}[\text{Fe}^{+3}]^2[\text{OH}^{-1}]^2; [\text{FeSO}_4] = 10^{2.3}[\text{Fe}^{+2}][\text{SO}_4^{-2}];$$

$$[\text{FeSO}_4^{+1}] = 10^{4.18}[\text{Fe}^{+3}][\text{SO}_4^{-2}]; [\text{Fe}(\text{SO}_4)_2^{-1}] =$$

$$10^{7.4}[\text{Fe}^{+3}][\text{SO}_4^{-2}]^2;$$

$$[\text{MnO}_4^{-1}] = [\text{Mn}^{+2}] \cdot 10^{5A(E - 1.507) + 8\text{pH}}; [\text{MnO}_4^{-2}] =$$

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

$$[\text{MnOH}^{+2}] = 10^{14.2}[\text{Mn}^{+3}][\text{OH}^{-1}] \quad (32)$$

Linear combination of balances

The T subsystem (II-1):

We get here the balances:

$$f_0 = \text{ChB}$$

$$N_2 - N_3 - N_7 - 2N_8 + N_{18} - N_{19} = 0$$

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

$$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_{18}n_{18} + 2N_{19}n_{19} = 2N_{03}$$

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

$$N_1 + N_2n_2 + N_3(1+n_3) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_{18}n_{18} + N_{19}(4+n_{19})$$

$$= 4N_{01} + N_{03} + 2N_{04}$$

$$-4f_4 = -4f(\text{CO}_3)$$

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

$$-f_7 = -f(\text{K})$$

$$N_{01} = N_{18}$$

$$-7f_8 = -7f(\text{Mn})$$

$$7N_{01} = 7N_{19}$$

$$f_{12} = 2f_2 - f_0 = 2f(O) - f(H)$$

$$-N_2 + N_3 + 4N_6 + 5N_7 + 6N_8 + 8N_{19} = 8N_{01} + 4N_{04}$$

$$f_{12} + f_0 - 4f_4 - f_7 - 7f_8 = 0 \Leftrightarrow (+1) \cdot f_1 + (-2) \cdot f_2 + (+4) \cdot f_4 + (+7) \cdot f_8 - f_0 = 0 \Leftrightarrow$$

$$(+1) \cdot f(H) + (-2) \cdot f(O) + (+4) \cdot f(CO_3) + (+7) \cdot f(Mn) - ChB = (33)$$

$$0 = 0$$

The coefficients/multipliers at the corresponding balances are equal to ON's of elements in the corresponding species.

The D subsystem (II-2): The D is identical here with D considered subsystem I-2, i.e., the relation 14 for the identity $0 = 0$ remains in force.

The D+T system (II-3):

For the D+T system we have the balances:

$$f_0 = ChB$$

$$N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 2N_9 + N_{10} + 3N_{12} + 2N_{13} + N_{14} + 4N_{15} + N_{16} - N_{17} + N_{18} - N_{19} - 2N_{20} +$$

$$3N_{21} + 2N_{22} + 2N_{23} + N_{24} = 0 \quad (34)$$

$$f_1 = f(H)$$

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

$$N_{10}(1+2n_{10}) + 2N_{11}n_{11} + 2N_{12}n_{12} + N_{13}(1+2n_{13}) + N_{14}(2+2n_{14}) +$$

$$N_{15}(2+2n_{15}) + 2N_{16}n_{16} + 2N_{17}n_{17} +$$

$$2N_{18}n_{18} + 2N_{19}n_{19} + 2N_{20}n_{20} + 2N_{21}n_{21} + N_{22}(1+2n_{22}) + 2N_{23}n_{23} +$$

$$N_{24}(1+2n_{24}) + 2N_{25}n_{25}$$

$$= 2N_{03} + 14N_{05} + 2N_{06} + 2N_{07}$$

$$f_2 = f(O)$$

$$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) +$$

$$N_7(3+n_7) + N_8(3+n_8) + N_9n_9 +$$

$$N_{10}(1+n_{10}) + N_{11}(4+n_{11}) + N_{12}n_{12} + N_{13}(1+n_{13}) + N_{14}(2+n_{14}) +$$

$$N_{15}(2+n_{15}) + N_{16}(4+n_{16}) + N_{17}(8+n_{17}) +$$

$$N_{18}n_{18} + N_{19}(4+n_{19}) + N_{20}(4+n_{20}) + N_{21}n_{21} + N_{22}(1+n_{22}) + N_{23}n_{23}$$

$$+ N_{24}(1+n_{24}) + N_{25}(4+n_{25})$$

$$= 4N_{01} + N_{03} + 2N_{04} + 11N_{05} + 4N_{06} + N_{07} + 2N_{08}$$

$$-f_3 = -f(SO_4)$$

$$N_{05} + N_{06} = N_4 + N_5 + N_{11} + N_{16} + 2N_{17} + N_{25} \quad (35)$$

$$-f_4 = -f(CO_3)$$

$$N_{04} + N_{08} = N_6 + N_7 + N_8 \quad (17)$$

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

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

$$-f_6 = -f(K)$$

$$N_{01} = N_{18} \quad (36)$$

$$-f_7 = -f(Mn)$$

$$N_{01} = N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} \quad (37)$$

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

$$-N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} + N_{13} +$$

$$2N_{14} + 2N_{15} + 8N_{16} + 16N_{17} +$$

$$8N_{19} + 8N_{20} + N_{22} + N_{24} + 8N_{25} = 8N_{01} + 4N_{04} + 8N_{05} + 6N_{06} +$$

$$4N_{08} \quad (38)$$

$$2 \cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4 - f_7 = 0 \Leftrightarrow (+1) \cdot f_1$$

$$+ (-2) \cdot f_2 + (+6) \cdot f_3 + (+4) \cdot f_4 + (+1) \cdot f_7 - f_0 = 0 \Leftrightarrow$$

$$(+1) \cdot f(H) + (-2) \cdot f(O) + (+6) \cdot f(SO_4) + (+4) \cdot f(CO_3) + (+1) \cdot f(K) - ChB = 0 \quad (39)$$

$$2(N_9 + N_{10} + N_{11}) + 3(N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17}) + 7N_{19} + 6N_{20} +$$

$$3(N_{21} + N_{22}) + 2(N_{23} + N_{24} + N_{25}) = 7N_{01} + 2N_{05} \quad (40)$$

Denoting the atomic numbers: $Z_{Fe} = 26$, $Z_{Mn} = 25$, from Equations: 16, 17 and 20, we obtain the balance

$$Z_{Fe} \cdot f_5 + Z_{Mn} \cdot f_8 - (2 \cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4 - f_7)$$

$$(Z_{Fe} - 2)(N_9 + N_{10} + N_{11}) + (Z_{Fe} - 3)(N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17}) +$$

$$(Z_{Mn} - 7)N_{19} + (Z_{Mn} - 6)N_{20} +$$

$$(Z_{Mn} - 3)(N_{21} + N_{22}) + (Z_{Mn} - 2)(N_{23} + N_{24} + N_{25}) = (Z_{Fe} - 2)N_{05} +$$

$$(Z_{Mn} - 7)N_{01} \quad (41)$$

Next, we can apply the combination of Equations 32, 16 and 30, giving the shortest form of GEB

$$3f_5 + 2f_8 - (2 \cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4 - f_7) = 0$$

$$(N_9 + N_{10} + N_{11}) - (5N_{19} + 4N_{20} + N_{21} + N_{22}) = N_{05} - 5N_{01} \quad (42)$$

From the linear combination of balances: 32, 16 and 30

$$5f_5 + f_8 + (3f_5 + 2f_8 - (2 \cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4 - f_7)) = 0 \Rightarrow$$

$$8f_5 + 3f_8 - (2 \cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4 - f_7) = 0 \quad (43)$$

we get the relation for GEB

$$N_{20} + 4(N_{21} + N_{22}) - (N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17}) = 0 \quad (44)$$

where the numbers of components: N_{01} for $KMnO_4$ and

N_{05} for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ are not involved explicitly. Applying the relations:

$$[x_i^{z_i}] \cdot (V_0 + V) = 10^3 \cdot \frac{N_i}{N_A}, \quad CV = 10^3 \cdot N_{01} / N_A, \quad C_0 V_0 = 10^3 \cdot N_{05} / N_A, \\ C_1 V = 10^3 \cdot N_{04} / N_A, \quad C_{01} V_0 = 10^3 \cdot N_{06} / N_A, \quad C_{02} V_0 = 10^3 \cdot N_{08} / N_A \quad (45)$$

in the balances derived above, we have the optional/equivalent equations for GEB :

$$- [H^{+1}] + [OH^{-1}] + 7[HSO_4^{-1}] + 8[SO_4^{-2}] + 4[H_2CO_3] + \\ 5[HCO_3^{-1}] + 6[CO_3^{-2}] + [FeOH^{+1}] + [FeSO_4] + [FeOH^{+2}] + \\ 2[Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + 8[FeSO_4^{+1}] + \\ 16[Fe(SO_4)_2^{-1}] + 8[MnO_4^{-1}] + 8[MnO_4^{-2}] + \\ [MnOH^{+2}] + [MnOH^{+1}] + 8[MnSO_4] \\ - (8CV + 4C_1V + 8C_0V_0 + 6C_{01}V_0 + 4C_{02}V_0) / (V_0 + V) = 0 \quad (38a)$$

$$2([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) + 3([Fe^{+3}] + [FeOH^{+2}] + \\ [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + \\ [Fe(SO_4)_2^{-1}] + 7[MnO_4^{-1}] + 6[MnO_4^{-2}] + 3([Mn^{+3}] + [MnOH^{+2}]) + \\ 2([Mn^{+2}] + [MnOH^{+1}] + [MnSO_4]) - (2C_0V_0 + 7CV) / (V_0 + V) = 0 \quad (40a)$$

$$(Z_{Fe}-2)([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) + (Z_{Fe}-3)([Fe^{+3}] + \\ [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + \\ [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}]) + (Z_{Mn}-7)[MnO_4^{-1}] + \\ (Z_{Mn}-6)[MnO_4^{-2}] + (Z_{Mn}-3)([Mn^{+3}] + [MnOH^{+2}]) + \\ (Z_{Mn}-2)([Mn^{+2}] + [MnOH^{+1}] + [MnSO_4]) \\ - ((Z_{Fe}-2)C_0V_0 + (Z_{Mn}-7)CV) / (V_0 + V) = 0 \quad (41a)$$

$$[Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] - (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + \\ [Mn^{+3}] + [MnOH^{+2}]) \\ - (C_0V_0 - 5CV) / (V_0 + V) = 0 \quad (42a)$$

$$[Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + \\ [Fe(SO_4)_2^{-1}] - \\ ([MnO_4^{-2}] + 4([Mn^{+3}] + [MnOH^{+2}])) = 0 \quad (44a)$$

In other words, the GEB can be chosen arbitrarily from the set of equivalent equations: 38a, 40a, 41a, 42a, 44a. Eq. 42a, as one of them, is completed by charge and concentration balances:

$$[H^{+1}] - [OH^{-1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] - [HCO_3^{-1}] - \\ 2[CO_3^{-2}] + 2[Fe^{+2}] + [FeOH^{+1}] + 3[Fe^{+3}] + 2[FeOH^{+2}] + \\ [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] - [Fe(SO_4)_2^{-1}] +$$

$$[K^{+1}] - [MnO_4^{-1}] - 2[MnO_4^{-2}] + 3[Mn^{+3}] + 2[MnOH^{+2}] + \\ 2[Mn^{+2}] + [MnOH^{+1}] = 0 \quad (34a)$$

$$[HSO_4^{-1}] + [SO_4^{-2}] + [FeSO_4] + [FeSO_4^{+1}] + 2[Fe(SO_4)_2^{-1}] + \\ [MnSO_4] \\ - (C_0 + C_{01})V_0 / (V_0 + V) = 0 \quad (35a)$$

$$[K^{+1}] = CV / (V_0 + V) \quad (36a)$$

$$[H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] = (C_{02}V_0 + C_1V) / (V_0 + V) \quad (17a)$$

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

$$[MnO_4^{-1}] + [MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}] + [Mn^{+2}] + \\ [MnOH^{+1}] + [MnSO_4] \\ - CV / (V_0 + V) = 0 \quad (37a)$$

The set of K=6 equations: 42a, 34a, 35a, 17a, 18a, 37a is taken for calculations; the equality (not equation!) 36a can enter immediately Eq. 34a, like a number. The number of equations is equal to the number of independent variables, considered as components of the vector:

$$\mathbf{x} = [x_1, \dots, x_6]^T = [E, \text{pH}, \text{pMn2}, \text{pFe2}, \text{pSO4}, \text{pH2CO3}]^T$$

where $\text{pMn2} = -\log[Mn^{+2}]$; other notations are as in Eq. 29.

Computer program

```
function F = Function_MnO4_Fe(x)
global V Vmin Vstep Vmax Vo C Co Ca H OH fi pH E
global Kw pKw A K logK
global HSO4 SO4 logHSO4 logSO4
global Mn7O4 Mn6O4 Mn3 Mn3OH
global logMn7O4 logMn6O4 logMn3 logMn3OH
global Mn2 Mn2OH Mn2SO4
global logMn2 logMn2OH logMn2SO4
global Fe2 Fe2OH Fe2SO4
global logFe2 logFe2OH logFe2SO4
global Fe3 Fe3OH Fe3OH2 Fe32OH2 Fe3SO4 Fe3SO42
global logFe3 logFe3OH logFe3OH2 logFe32OH2 logFe3SO4
logFe3SO42
pH=x(1);
E=x(2);
```

$$\text{Mn}2=10.^{\wedge-x(3)};$$

$$\text{Fe}2=10.^{\wedge-x(4)};$$

$$\text{SO}4=10.^{\wedge-x(5)};$$

$$\text{H}=10.^{\wedge-\text{pH}};$$

$$\text{pKw}=14;$$

$$\text{Kw}=10.^{\wedge-14};$$

$$\text{OH}=\text{Kw}/\text{H};$$

$$\text{A}=16.9;$$

$$\text{ZFe}=26;$$

$$\text{ZMn}=25;$$

$$\text{Mn}7\text{O}4=\text{Mn}2.^*10.^{\wedge(5.^*A.^*(E-1.507)+8.^*\text{pH})};$$

$$\text{Mn}6\text{O}4=\text{Mn}2.^*10.^{\wedge(4.^*A.^*(E-1.743)+8.^*\text{pH})};$$

$$\text{Mn}3=\text{Mn}2.^*10.^{\wedge(A.^*(E-1.509))};$$

$$\text{Fe}3=\text{Fe}2.^*10.^{\wedge(A.^*(E-0.771))};$$

$$\text{HSO}4=10.^{\wedge 1.8.^*H.^*\text{SO}4};$$

$$\text{Fe}2\text{OH}=10.^{\wedge 4.5.^*\text{Fe}2.^*\text{OH}};$$

$$\text{Fe}2\text{SO}4=10.^{\wedge 2.3.^*\text{Fe}2.^*\text{SO}4};$$

$$\text{Fe}3\text{OH}=10.^{\wedge 11.0.^*\text{Fe}3.^*\text{OH}};$$

$$\text{Fe}3\text{OH}2=10.^{\wedge 21.7.^*\text{Fe}3.^*\text{OH}.\wedge 2};$$

$$\text{Fe}32\text{OH}2=10.^{\wedge 25.1.^*\text{Fe}3.\wedge 2.^*\text{OH}.\wedge 2};$$

$$\text{Fe}3\text{SO}4=10.^{\wedge 4.18.^*\text{Fe}3.^*\text{SO}4};$$

$$\text{Fe}3\text{SO}42=10.^{\wedge 7.4.^*\text{Fe}3.^*\text{SO}4.\wedge 2};$$

$$\text{Mn}2\text{OH}=10.^{\wedge 3.4.^*\text{Mn}2.^*\text{OH}};$$

$$\text{Mn}2\text{SO}4=10.^{\wedge 2.28.^*\text{Mn}2.^*\text{SO}4};$$

$$\text{Mn}3\text{OH}=10.^{\wedge 14.2.^*\text{Mn}3.^*\text{OH}};$$

$$\text{K}=\text{C}.*\text{V}/(\text{V}0+\text{V});$$

%Charge balance

$$\text{F}=[(\text{H}-\text{OH}+\text{K}-\text{HSO}4-2.^*\text{SO}4-\text{Mn}7\text{O}4-$$

$$2.^*\text{Mn}6\text{O}4+3.^*\text{Mn}3+2.^*\text{Mn}3\text{OH}...$$

$$+2.^*\text{Mn}2+\text{Mn}2\text{OH}+2.^*\text{Fe}2+\text{Fe}2\text{OH}+3.^*\text{Fe}3+2.^*\text{Fe}3\text{OH}+\text{Fe}3$$

$$\text{OH}2...$$

$$+4.^*\text{Fe}32\text{OH}2+\text{Fe}3\text{SO}4-\text{Fe}3\text{SO}42);$$

%Concentration balance of Mn

$$(\text{Mn}7\text{O}4+\text{Mn}6\text{O}4+\text{Mn}3+\text{Mn}3\text{OH}+\text{Mn}2+\text{Mn}2\text{OH}+\text{Mn}2\text{SO}4-$$

$$\text{C}.*\text{V}/(\text{V}0+\text{V}));$$

%Concentration balance of Fe

$$(\text{Fe}2+\text{Fe}2\text{OH}+\text{Fe}2\text{SO}4+\text{Fe}3+\text{Fe}3\text{OH}+\text{Fe}3\text{OH}2+2.^*\text{Fe}32\text{OH}2...$$

$$+\text{Fe}3\text{SO}4+\text{Fe}3\text{SO}42-\text{Co}.*\text{V}0)/(\text{V}0+\text{V}));$$

%Concentration balance of S

$$(\text{HSO}4+\text{SO}4+\text{Mn}2\text{SO}4+\text{Fe}2\text{SO}4+\text{Fe}3\text{SO}4+2.^*\text{Fe}3\text{SO}42-$$

$$(\text{Co}+\text{Ca})*\text{V}0)/(\text{V}0+\text{V}));$$

%Electron balance

$$((\text{ZMn}-7)^*.\text{Mn}7\text{O}4+(\text{ZMn}-6)^*.\text{Mn}6\text{O}4+(\text{ZMn}-$$

$$3)^*.\text{Mn}3+\text{Mn}3\text{OH})...$$

$$+(\text{ZMn}-2)^*.\text{Mn}2+\text{Mn}2\text{OH}+\text{Mn}2\text{SO}4)+(\text{ZFe}-$$

$$2)^*.\text{Fe}2+\text{Fe}2\text{OH}+\text{Fe}2\text{SO}4)...$$

$$+(\text{ZFe}-3)^*.\text{Fe}3+\text{Fe}3\text{OH}+\text{Fe}3\text{OH}2+\text{Fe}32\text{OH}2+\text{Fe}3\text{SO}4+\text{Fe}3$$

$$\text{SO}42)...$$

$$-((\text{ZFe}-2)^*.\text{Co}.*\text{V}0+(\text{ZMn}-7)^*.\text{C}.*\text{V}0)/(\text{V}0+\text{V}));$$

$$\log\text{Mn}2=\log10(\text{Mn}2);$$

$$\log\text{Mn}2\text{OH}=\log10(\text{Mn}2\text{OH});$$

$$\log\text{Mn}2\text{SO}4=\log10(\text{Mn}2\text{SO}4);$$

$$\log\text{Mn}3=\log10(\text{Mn}3);$$

$$\log\text{Mn}3\text{OH}=\log10(\text{Mn}3\text{OH});$$

$$\log\text{Mn}6\text{O}4=\log10(\text{Mn}6\text{O}4);$$

$$\log\text{Mn}7\text{O}4=\log10(\text{Mn}7\text{O}4);$$

$$\log\text{Fe}2=\log10(\text{Fe}2);$$

$$\log\text{Fe}2\text{OH}=\log10(\text{Fe}2\text{OH});$$

$$\log\text{Fe}2\text{SO}4=\log10(\text{Fe}2\text{SO}4);$$

$$\log\text{Fe}3=\log10(\text{Fe}3);$$

$$\log\text{Fe}3\text{OH}=\log10(\text{Fe}3\text{OH});$$

$$\log\text{Fe}3\text{OH}2=\log10(\text{Fe}3\text{OH}2);$$

$$\log\text{Fe}32\text{OH}2=\log10(\text{Fe}32\text{OH}2);$$

$$\log\text{Fe}3\text{SO}4=\log10(\text{Fe}3\text{SO}4);$$

$$\log\text{Fe}3\text{SO}42=\log10(\text{Fe}3\text{SO}42);$$

$$\log\text{HSO}4=\log10(\text{HSO}4);$$

$$\log\text{SO}4=\log10(\text{SO}4);$$

$$\log\text{K}=\log10(\text{K});$$

Graphical presentation of results and discussion

The results of calculations realized for D+T system with use of MATLAB are presented in Figures 5-8 [11,39]. Figures 5a,b and 6a,b and 7 were plotted at $V_0=100$, $C = 0.02$, $C_0=0.01$, $C_{01}=0.5$, $C_0 = 0.001$. The jump on the curve in Figure 5a occurs at $\Phi = \Phi_{eq} = \frac{1}{5}$, i.e., at the equivalent point where $C \cdot V_{eq} = \frac{1}{5} \cdot C_0 \cdot V_0$. From Figure 6a we see that $[Fe^{+3}] \ll [FeSO_4^{+1}] \ll [Fe(SO_4)_2^{-1}]$. Note that $MnOH^{+2}$ and Mn^{+3} (not MnO_4^{-1}) are the predominating manganese species, immediately after crossing the related equivalence point (Figure 6b). Some points from the vicinity of equivalence point are presented in Table 2.

The titration curves $E = E(\Phi)$ for this D+T system, plotted at different concentrations C_{01} of H_2SO_4 contained in the titrand (D), are shown in Figure 7a. Some fragments of the curves,

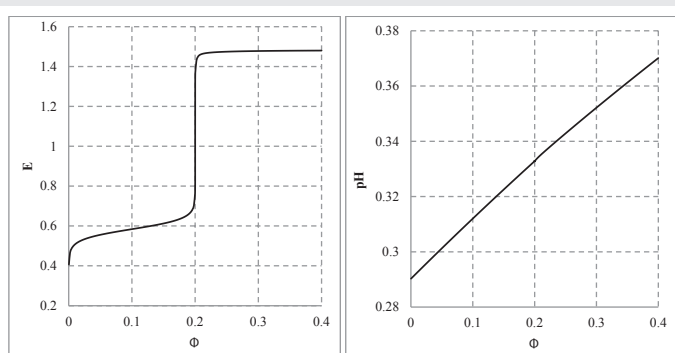


Figure 5: System II-3: The relationships: (5a) $E = E(\Phi)$ and (5b) $pH = pH(\Phi)$ plotted at $V_0=100$, $C = 0.02$, $C_0=0.01$, $C_{01}=0.5$, $C_1=C_{02}=0$.

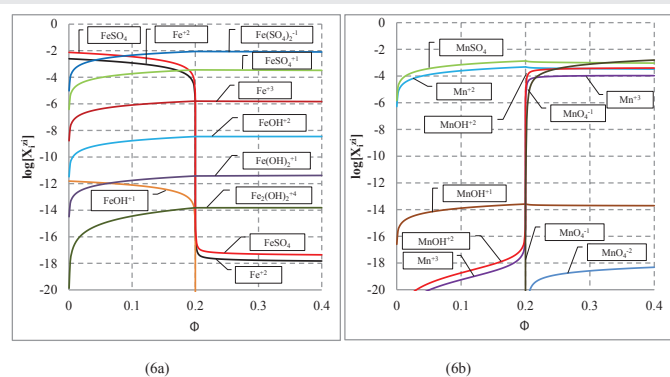


Figure 6: System II-3: The speciation curves plotted for (6a) Mn and (6b) Fe species at $V_0 = 100$, $C = 0.02$, $C_{01} = C_{02} = 0.02$; $C_{03} = 0.5$; $C_1 = C_{04} = 0.001$.

Table 2: System II-3: The pairs of selected (Φ , E) values from the vicinity of $\Phi_{eq} = 0.2 = \frac{1}{5}$; $V_0=100$, $C_0=0.01$, $C=0.02$, $C_{01} = 0.5$, $C_{02} = C_1 = 0$.

Φ	E, mV
0.19800	0.701
0.19900	0.719
0.19980	0.761
0.19990	0.778
0.19998	0.820
0.20000	1.034
0.20002	1.323
0.20010	1.365
0.20020	1.382
0.20200	1.442

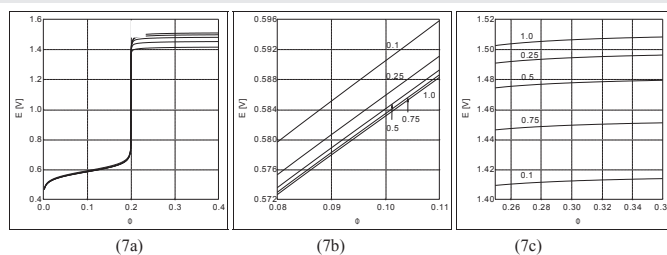


Figure 7: System II-3: The collected $E = E(\Phi)$ curves (7a) plotted at $V_0 = 100$, $C_0 = 0.01$, $C = 0.02$, $C_{02} = C_1 = 0.001$ at different C_{01} values, indicated at their enlarged fragments relating to: (7b) $\Phi < \Phi_{eq}$, (7c) $\Phi > \Phi_{eq}$.

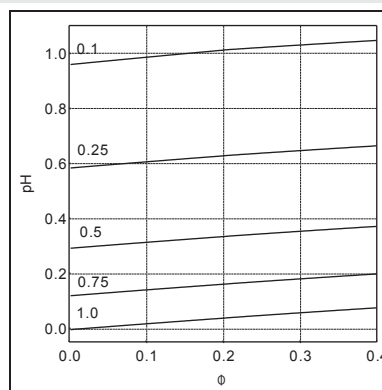


Figure 8: System II-3: The plots for $pH = pH(\Phi)$ relationship plotted at $V_0 = 100$, $C_0 = 0.01$, $C = 0.02$, $C_{02} = C_1 = 0.001$, and different C_{01} values indicated at the corresponding lines in Figure 7.

related to $\Phi < \Phi_{eq}$ and $\Phi > \Phi_{eq}$ are presented, in extended scale, in Figures 7b,c. The related plots for $pH = pH(\Phi)$ relationships are given in Figure 8.

System III

We consider here non-redox subsystems:

(III-1) T (V) subsystem, composed of $KMnO_4 (N_{01}) + H_2O (N_{02}) + CO_2 (N_{03})$;

(III-2) D (V_0) subsystem, composed of $FeSO_4 \cdot 7H_2O (N_{04}) + H_2C_2O_4 \cdot 2H_2O (N_{05}) + H_2SO_4 (N_{06}) + H_2O (N_{07}) + CO_2 (N_{08})$;

and

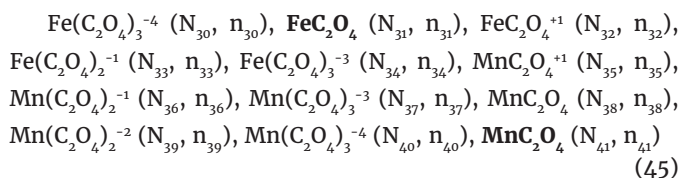
(III-3) D+T (V_0+V) redox system, as the mixture of D and T, where the following species are formed:

$H_2O (N_1)$, $H^{+1} (N_2, n_2)$, $OH^{-1} (N_3, n_3)$, $HSO_4^{-1} (N_4, n_4)$, $SO_4^{-2} (N_5, n_5)$, $H_2CO_3 (N_6, n_6)$, $HCO_3^{-1} (N_7, n_7)$,

$CO_3^{-2} (N_8, n_8)$, $Fe^{+2} (N_9, n_9)$, $FeOH^{+1} (N_{10}, n_{10})$, $FeSO_4 (N_{11}, n_{11})$, $Fe^{+3} (N_{12}, n_{12})$, $FeOH^{+2} (N_{13}, n_{13})$,

$Fe(OH)_2^{+1} (N_{14}, n_{14})$, $Fe_2(OH)_2^{+4} (N_{15}, n_{15})$; $FeSO_4^{+1} (N_{16}, n_{16})$, $Fe(SO_4)_2^{-1} (N_{17}, n_{17})$, $K^{+1} (N_{18}, n_{18})$,

$MnO_4^{-1} (N_{19}, n_{19})$, $MnO_4^{-2} (N_{20}, n_{20})$, $Mn^{+3} (N_{21}, n_{21})$, $MnOH^{+2} (N_{22}, n_{22})$, $Mn^{+2} (N_{23}, n_{23})$, $MnOH^{+1} (N_{24}, n_{24})$, $MnSO_4 (N_{25}, n_{25})$, $H_2C_2O_4 (N_{26}, n_{26})$, $HC_2O_4^{-1} (N_{27}, n_{27})$, $C_2O_4^{-2} (N_{28}, n_{28})$, $Fe(C_2O_4)_2^{-2} (N_{29}, n_{29})$,



Molecules of the (pre-assumed) precipitates of the oxalates are written in bold: **FeC₂O₄** and **MnC₂O₄**.

As results from the list (45) of species, the components of D and D+T system can interact, forming soluble complexes; insoluble complexes (precipitates of oxalates) can also (potentially) be formed. Precipitation of **MnO₂** and other solid phases is not possible at low pH value and high buffer capacity of the mixture, resulting from presence of an excess of H₂SO₄.

$$[\text{C}_2\text{O}_4^{-2}] = 10^{-5.2} \cdot [\text{H}_2\text{C}_2\text{O}_4] / [\text{H}^+]^2 = 10^{2\text{pH} - 5.2} \cdot [\text{H}_2\text{C}_2\text{O}_4]; [\text{HC}_2\text{O}_4^{-1}] = 10^{3.8} \cdot [\text{H}^+] [\text{C}_2\text{O}_4^{-2}].$$

From $2\text{H}_2\text{CO}_3 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$ ($E_0 = -0.386$) we get

$$[\text{H}_2\text{CO}_3] = [\text{H}_2\text{C}_2\text{O}_4]^{0.5} \cdot 10^{A(E+0.396) + \text{pH}} \text{ and then:}$$

$$[\text{CO}_3^{-2}] = 10^{-16.4} \cdot [\text{H}_2\text{CO}_3] / [\text{H}^+]^2 = 10^{2\text{pH} - 16.4} \cdot [\text{H}_2\text{CO}_3]; [\text{HCO}_3^{-1}] = 10^{10.1} \cdot [\text{H}^+] [\text{CO}_3^{-2}].$$

Further equilibrium data are involved in the relationships:

$$[\text{HSO}_4^{-1}] = 10^{1.8} \cdot [\text{H}^+] [\text{SO}_4^{-2}]; [\text{FeOH}^{+1}] = 10^{4.5} \cdot [\text{Fe}^{+2}] [\text{OH}^{-1}];$$

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

$$10^{21.7} \cdot [\text{Fe}^{+3}] [\text{OH}^{-1}]^2; [\text{Fe}_2(\text{OH})_2^{+4}] = 10^{25.1} \cdot [\text{Fe}^{+3}]^2 [\text{OH}^{-1}]^2;$$

$$[\text{MnOH}^{+1}] = 10^{3.4} \cdot [\text{Mn}^{+2}] [\text{OH}^{-1}]; [\text{FeSO}_4] = 10^{2.3} \cdot [\text{Fe}^{+2}] [\text{SO}_4^{-2}];$$

$$[\text{FeSO}_4^{+1}] = 10^{4.18} \cdot [\text{Fe}^{+3}] [\text{SO}_4^{-2}]; [\text{Fe}(\text{SO}_4)_2^{-1}] =$$

$$10^{7.4} \cdot [\text{Fe}^{+3}] [\text{SO}_4^{-2}]^2; [\text{MnSO}_4] = 10^{2.28} \cdot [\text{Mn}^{+2}] [\text{SO}_4^{-2}];$$

$$[\text{Fe}(\text{C}_2\text{O}_4)_2^{-2}] = 10^{4.52} \cdot [\text{Fe}^{+2}] [\text{C}_2\text{O}_4^{-2}]^2; [\text{Fe}(\text{C}_2\text{O}_4)_3^{-4}] =$$

$$10^{5.22} \cdot [\text{Fe}^{+2}] [\text{C}_2\text{O}_4^{-2}]^3; [\text{FeC}_2\text{O}_4^{+1}] = 10^{7.53} \cdot [\text{Fe}^{+3}] [\text{C}_2\text{O}_4^{-2}];$$

$$[\text{Fe}(\text{C}_2\text{O}_4)_2^{-1}] = 10^{13.64} \cdot [\text{Fe}^{+3}] [\text{C}_2\text{O}_4^{-2}]^2; [\text{Fe}(\text{C}_2\text{O}_4)_2^{-3}] =$$

$$10^{18.49} \cdot [\text{Fe}^{+3}] [\text{C}_2\text{O}_4^{-2}]^3; [\text{MnC}_2\text{O}_4] = 10^{3.82} \cdot [\text{Mn}^{+2}] [\text{C}_2\text{O}_4^{-2}];$$

$$[\text{Mn}(\text{C}_2\text{O}_4)_2^{-2}] = 10^{5.25} \cdot [\text{Mn}^{+2}] [\text{C}_2\text{O}_4^{-2}]^2; [\text{MnC}_2\text{O}_4^{+1}] =$$

$$10^{9.98} \cdot [\text{Mn}^{+3}] [\text{C}_2\text{O}_4^{-2}]; [\text{Mn}(\text{C}_2\text{O}_4)_2^{-1}] = 10^{16.57} \cdot [\text{Mn}^{+3}] [\text{C}_2\text{O}_4^{-2}]^2;$$

$$[\text{Mn}(\text{C}_2\text{O}_4)_3^{-3}] = 10^{19.42} \cdot [\text{Mn}^{+3}] [\text{C}_2\text{O}_4^{-2}]^3; [\text{MnO}_4^{-1}] =$$

$$[\text{Mn}^{+2}] \cdot 10^{5A(E - 1.507) + 8\text{pH}}; [\text{MnO}_4^{-2}] = [\text{Mn}^{+2}] \cdot 10^{4A(E - 1.743) + 8\text{pH}};$$

$$[\text{Mn}^{+3}] = [\text{Mn}^{+2}] \cdot 10^{A(E - 1.509)}; [\text{Fe}^{+3}] = [\text{Fe}^{+2}] \cdot 10^{A(E - 0.771)}.$$

The relations for solubility products for **FeC₂O₄** and **MnC₂O₄** are as follows:

$$K_{\text{sol1}} = [\text{Fe}^{+2}] [\text{C}_2\text{O}_4^{-2}] \quad (\text{p}K_{\text{sol1}} = 6.7),$$

$$K_{\text{sol2}} = [\text{Mn}^{+2}] [\text{C}_2\text{O}_4^{-2}] \quad (\text{p}K_{\text{sol2}} = 5.3) \quad (46)$$

Linear combination of balances

The T subsystem (III-1): The T subsystem is identical with the T subsystem II-1.

The D subsystem (III-2):

On the basis of the set of species in (45), we formulate the balances:

$$f_0 = \text{ChB}$$

$$\begin{aligned} & \text{N}_2 - \text{N}_3 - \text{N}_4 - 2\text{N}_5 - \text{N}_7 - 2\text{N}_8 + 2\text{N}_9 + \text{N}_{10} + \text{N}_{24} - \text{N}_{27} - 2\text{N}_{28} \\ & - 2\text{N}_{29} - 4\text{N}_{30} = 0 \end{aligned}$$

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

$$\begin{aligned} & 2\text{N}_1 + \text{N}_2(1+2\text{n}_2) + \text{N}_3(1+2\text{n}_3) + \text{N}_4(1+2\text{n}_4) + 2\text{N}_5\text{n}_5 + \text{N}_6(2+2\text{n}_6) \\ & + \text{N}_7(1+2\text{n}_7) + 2\text{N}_8\text{n}_8 + 2\text{N}_9\text{n}_9 + \end{aligned}$$

$$\begin{aligned} & \text{N}_{10}(1+2\text{n}_{10}) + 2\text{N}_{11}\text{n}_{11} + 2\text{N}_{23}\text{n}_{23} + \text{N}_{24}(1+2\text{n}_{24}) + \text{N}_{26}(2+2\text{n}_{26}) + \\ & \text{N}_{27}(1+2\text{n}_{27}) + 2\text{N}_{28}\text{n}_{28} + 2\text{N}_{29}\text{n}_{29} + \end{aligned}$$

$$2\text{N}_{30}\text{n}_{30} + \text{a}_1 \cdot 2\text{N}_{31}\text{n}_{31} = 14\text{N}_{04} + 6\text{N}_{05} + 2\text{N}_{06} + 2\text{N}_{07}$$

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

$$\begin{aligned} & \text{N}_1 + \text{N}_2\text{n}_2 + \text{N}_3(1+\text{n}_3) + \text{N}_4(4+\text{n}_4) + \text{N}_5(4+\text{n}_5) + \text{N}_6(3+\text{n}_6) + \\ & \text{N}_7(3+\text{n}_7) + \text{N}_8(3+\text{n}_8) + \text{N}_9\text{n}_9 + \text{N}_{10}(1+\text{n}_{10}) + \text{N}_{11}(4+\text{n}_{11}) + \text{N}_{23}\text{n}_{23} + \\ & \text{N}_{24}(1+\text{n}_{24}) + \text{N}_{26}(4+\text{n}_{26}) + \text{N}_{27}(4+\text{n}_{27}) + \text{N}_{28}(4+\text{n}_{28}) + \text{N}_{29}(8+\text{n}_{29}) \\ & + \text{N}_{30}(12+\text{n}_{30}) + \text{a}_1 \cdot \text{N}_{31}(4+\text{n}_{31}) = 11\text{N}_{04} + 6\text{N}_{05} + 4\text{N}_{06} + \text{N}_{07} + 2\text{N}_{08} \end{aligned}$$

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

$$\text{N}_{04} + \text{N}_{06} = \text{N}_4 + \text{N}_5 + \text{N}_{11}$$

$$-f_4 = -f(\text{C}_2\text{O}_4)$$

$$\text{N}_{05} = \text{N}_{26} + \text{N}_{27} + \text{N}_{28} + \text{N}_{29} + \text{N}_{30} + \text{a}_1 \cdot \text{N}_{31}$$

$$-f_5 = -f(\text{CO}_3)$$

$$\text{N}_{08} = \text{N}_6 + \text{N}_7 + \text{N}_8$$

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

$$\text{N}_{04} = \text{N}_9 + \text{N}_{10} + \text{N}_{11} + \text{N}_{29} + \text{N}_{30} + \text{a}_1 \cdot \text{N}_{31}$$

Then we have:

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

$$\begin{aligned} & -\text{N}_2 + \text{N}_3 + 7\text{N}_4 + 8\text{N}_5 + 4\text{N}_6 + 5\text{N}_7 + 6\text{N}_8 + \text{N}_{10} + 8\text{N}_{11} + \text{N}_{24} + \\ & 6\text{N}_{26} + 7\text{N}_{27} + 8\text{N}_{28} \end{aligned}$$

$$+ 16\text{N}_{29} + 24\text{N}_{30} + \text{a}_1 \cdot 8\text{N}_{31} = 8\text{N}_{04} + 6\text{N}_{05} + 6\text{N}_{06} + 4\text{N}_{08}$$

$$f_{12} + f_0 - 6 \cdot f_3 - 3 \cdot f_4 - 4 \cdot f_5 - 2 \cdot f_6 = 0 \Rightarrow$$

$$\begin{aligned} & (+1) \cdot f_1 + (-2) \cdot f_2 + (+6) \cdot f_3 + 2 \cdot (+3) \cdot f_4 + (+4) \cdot f_5 + (+2) \cdot f_6 - f_0 = \\ & 0 \Rightarrow \end{aligned}$$

$$\begin{aligned} & (+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+6) \cdot f(\text{SO}_4) + 2 \cdot (+3) \cdot f(\text{C}_2\text{O}_4) + \\ & (+4) \cdot f(\text{CO}_3) + (+2) \cdot f(\text{Fe}) - \text{ChB} = 0 \end{aligned} \quad (47)$$

$$0 = 0$$

This means that the D is a non-redox system.

The D+T system (III-3):

Three electron-active elements: Fe, C and Mn are involved in this system. Denoting atomic numbers: $Z_C = 6$ for C, $Z_{Mn} = 25$ for Mn, $Z_{Fe} = 26$ for Fe, the resulting GEB is written according to Approach I as follows:

$$\begin{aligned}
 & (Z_{Fe}-2)([Fe^{+2}] + [FeOH^{+1}] + [FeSO_4]) + (Z_{Fe}-3)([Fe^{+3}] + \\
 & [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] + \\
 & [Fe(SO_4)_2^{-1}] + (Z_{Fe}-2 + 4 \cdot (Z_C-3))[Fe(C_2O_4)_2^{-2}] + \\
 & (Z_{Fe}-2 + 6 \cdot (Z_C-3))[Fe(C_2O_4)_3^{-4}] + (Z_{Fe}-3 + 2 \cdot (Z_C-3))[FeC_2O_4^{+1}] + \\
 & (Z_{Fe}-3 + 4 \cdot (Z_C-3))[Fe(C_2O_4)_2^{-1}] + (Z_{Fe}-3 + 6 \cdot (Z_C-3)) \\
 & [Fe(C_2O_4)_3^{-3}] + \\
 & 2(Z_C-3)([H_2C_2O_4] + [HC_2O_4^{-1}] + [C_2O_4^{-2}]) + \\
 & (Z_C-4)([H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}]) + (Z_{Mn}-7)[MnO_4^{-1}] + \\
 & (Z_{Mn}-6)[MnO_4^{-2}] + (Z_{Mn}-3)([Mn^{+3}] + [MnOH^{+2}]) + \\
 & (Z_{Mn}-3 + 2 \cdot (Z_C-3))[MnC_2O_4^{+1}] + (Z_{Mn}-3 + 4 \cdot (Z_C-3)) \\
 & [Mn(C_2O_4)_2^{-1}] + \\
 & (Z_{Mn}-3 + 6 \cdot (Z_C-3))[Mn(C_2O_4)_3^{-3}] + (Z_{Mn}-2)([Mn^{+2}] + \\
 & [MnOH^{+1}] + \\
 & [MnSO_4]) + (Z_{Mn}-2 + 2 \cdot (Z_C-3))[MnC_2O_4] + \\
 & (Z_{Mn}-2 + 4 \cdot (Z_C-3))[Mn(C_2O_4)_2^{-2}] + (Z_{Mn}-2 + 6 \cdot (Z_C-3)) \\
 & [Mn(C_2O_4)_3^{-4}] + \\
 & a_1 \cdot (Z_{Fe}-2 + 2 \cdot (Z_C-3))[FeC_2O_4] + a_2 \cdot (Z_{Mn}-2 + 2 \cdot (Z_C-3)) \\
 & [MnC_2O_4] \\
 & = ((Z_{Fe}-2)C_{01}V_0 + 2 \cdot (Z_C-3)C_{02}V_0 + (Z_C-4)(C_{04}V_0 + C_1V) + \\
 & (Z_{Mn}-7)CV)/(V_0+V) \tag{48}
 \end{aligned}$$

Moreover, we write the charge balance

$$\begin{aligned}
 & [H^{+1}] - [OH^{-1}] + [K^{+1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] - [HC_2O_4^{-1}] - \\
 & 2[C_2O_4^{-2}] - [MnO_4^{-1}] - 2[MnO_4^{-2}] + 3[Mn^{+3}] + 2[MnOH^{+2}] + \\
 & [MnC_2O_4^{+1}] - [Mn(C_2O_4)_2^{-1}] - 3[Mn(C_2O_4)_3^{-3}] + 2[Mn^{+2}] + \\
 & [MnOH^{+1}] - 2[Mn(C_2O_4)_2^{-2}] - 4[Mn(C_2O_4)_3^{-4}] + 2[Fe^{+2}] + \\
 & [FeOH^{+1}] - 2[Fe(C_2O_4)_2^{-2}] - 4[Fe(C_2O_4)_3^{-4}] + 3[Fe^{+3}] + \\
 & 2[FeOH^{+2}] + [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] - \\
 & [Fe(SO_4)_2^{-1}] + [FeC_2O_4^{+1}] - [Fe(C_2O_4)_2^{-1}] - 3[Fe(C_2O_4)_3^{-3}] = 0 \tag{49}
 \end{aligned}$$

and concentration balances for Fe (Eq. 50), Mn (Eq. 51), C (Eq. 52) and SO_4 (Eq. 53):

$$\begin{aligned}
 & [Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] + [Fe(C_2O_4)_2^{-2}] + [Fe(C_2O_4)_3^{-4}] + \\
 & [Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] +
 \end{aligned}$$

$$\begin{aligned}
 & [Fe(SO_4)_2^{-1}] + [FeC_2O_4^{+1}] + [Fe(C_2O_4)_2^{-1}] + [Fe(C_2O_4)_3^{-3}] + \\
 & a_1 \cdot [FeC_2O_4] = C_{01}V_0/(V_0+V) \tag{50}
 \end{aligned}$$

$$\begin{aligned}
 & [MnO_4^{-1}] + [MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}] + [MnC_2O_4^{+1}] + \\
 & [Mn(C_2O_4)_2^{-1}] + [Mn(C_2O_4)_3^{-3}] + [Mn^{+2}] + [MnOH^{+1}] + \\
 & [MnSO_4] + [MnC_2O_4] + [Mn(C_2O_4)_2^{-2}] + [Mn(C_2O_4)_3^{-4}] + \\
 & a_2 \cdot [MnC_2O_4] = CV/(V_0+V) \tag{51}
 \end{aligned}$$

$$\begin{aligned}
 & 2[H_2C_2O_4] + 2[HC_2O_4^{-1}] + 2[C_2O_4^{-2}] + [H_2CO_3] + [HCO_3^{-1}] + \\
 & [CO_3^{-2}] + 2 \cdot [MnC_2O_4^{+1}] + 4 \cdot [Mn(C_2O_4)_2^{-1}] + 6 \cdot [Mn(C_2O_4)_3^{-3}] + \\
 & 2 \cdot [MnC_2O_4] + 4 \cdot [Mn(C_2O_4)_2^{-2}] + 6 \cdot [Mn(C_2O_4)_3^{-4}] + \\
 & 4 \cdot [Fe(C_2O_4)_2^{-2}] + 6 \cdot [Fe(C_2O_4)_3^{-4}] + 2 \cdot [FeC_2O_4^{+1}] + \\
 & 4 \cdot [Fe(C_2O_4)_2^{-1}] + 6 \cdot [Fe(C_2O_4)_3^{-3}] + 2a_1 \cdot [FeC_2O_4] + \\
 & 2a_2 \cdot [MnC_2O_4] = (2C_{02}V_0 + C_{04}V_0 + C_1V)/(V_0+V) \tag{52}
 \end{aligned}$$

$$\begin{aligned}
 & [HSO_4^{-1}] + [SO_4^{-2}] + [MnSO_4] + [FeSO_4] + [FeSO_4^{+1}] + \\
 & 2[Fe(SO_4)_2^{-1}] = (C_{01}V_0 + C_{03}V_0)/(V_0+V) \tag{53}
 \end{aligned}$$

i.e. together 6 balances. The relation $[K^{+1}] = CV/(V_0+V)$ is not considered as a concentration balance; because at defined C, V_0 and V values, it is a number (not variable) and – as such – it enters the charge balance. We have $a_1 = 0$ if FeC_2O_4 is not an equilibrium solid phase, and $a_2 = 0$ if MnC_2O_4 is not an equilibrium solid phase; $a_1 = 1$ if the solubility product for FeC_2O_4 is crossed, and $a_1 = 1$ if the solubility product for MnC_2O_4 is crossed.

Graphical presentation of results and discussion

The results of calculations made in the system III-3 are presented graphically in Figures 9, 10. The titration curves obtained at $V_0=100$, $C_0 = 0.01$, $C=0.02$, $C_{03} = 0.5$, $C_1=C_{04}=0.001$, and different pairs of (C_{01}, C_{02}) values, are plotted in Figure 9a. The related pH changes are presented in Figure 9b. Table 2 gives the co-ordinates of some points (V_j, E_j) selected from the vicinity of equivalence points indicated by potential jumps on the curves $E = E(V)$ obtained at $C_{01}=C_{02} = 0.01$ (see Figure 9a). The speciation curves for Fe and Mn species related to $C_{01} = C_{02} = 0.01$ are presented in Figures 10a,b.

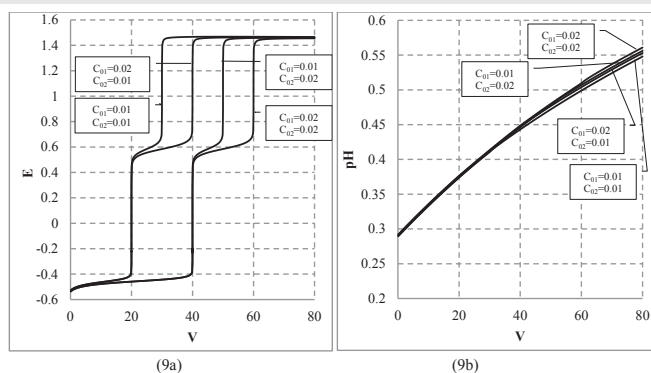


Figure 9: System III-3: The relationships: (9a) $E = E(V)$; (9b) $pH = pH(V)$ plotted at: $V_0 = 100$, $C = 0.02$, $C_{03} = 0.5$, $C_1 = C_{04} = 0$, and indicated pairs of C_{01} and C_{02} values.

There are the 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 $C_{01} = 0.02$, $C_{02} = 0.02$. This agrees exactly with the position of the points in Figure 9a.

The positions of potential E jumps can/should be compared with E jumps on the plots of titration curves obtained for

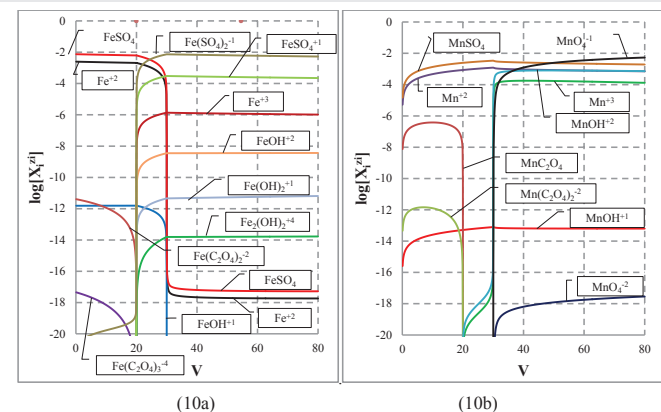


Figure 10: System III-3: The speciation curves plotted for (10a) Fe and (10b) Mn species at $V_0 = 100$, $C = 0.02$, $C_{01} = C_{02} = 0.02$, $C_{03} = 0.5$, $C_1 = C_{04} = 0$.

Table 3: System III-3: Some points (V , E) taken from the vicinity of jumps on the curves $E = E(V)$ presented in Fig. 9 at $C_{01} = C_{02} = 0.01$.

$C_{01} = 0.01, C_{02} = 0.01$			
V [mL]	E [V]	V [mL]	E [V]
19.5	-0.4123	29.5	0.6600
19.6	-0.4093	29.6	0.6660
19.7	-0.4055	29.7	0.6737
19.8	-0.4002	29.8	0.6844
19.9	-0.3912	29.9	0.7024
19.999	-0.3320	29.99991	0.8827
19.9995	-0.3231	29.99995	0.8978
19.9999	-0.3025	29.99999	0.9391
20	-0.2382	30	1.0430
20.0001	0.2881	30.00001	1.1600
20.0005	0.3294	30.00005	1.2013
20.001	0.3472	30.0001	1.2191
20.1	0.4657	30.1	1.3967
20.2	0.4838	30.2	1.4148
20.3	0.4944	30.3	1.4254
20.4	0.5021	30.4	1.4328
20.5	0.5081	30.5	1.4382

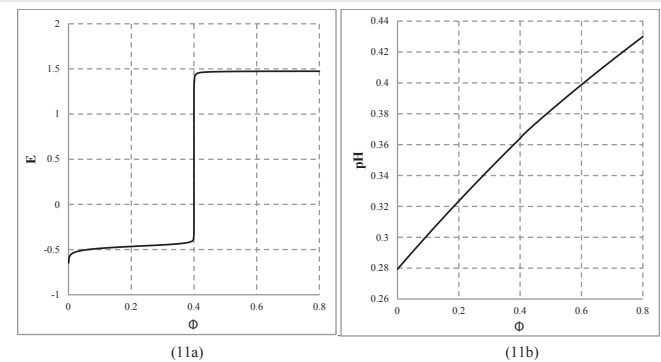


Figure 11: System III-3a: The relationships: (11a) $E = E(\Phi)$; (11b) $pH = pH(\Phi)$ plotted at: $V_0 = 100$, $C = 0.02$, $C_{03} = 0.5$, $C_1 = C_{04} = 0$.

Table 4: System III-3a: The pairs of selected (Φ , E) values from the vicinity of $\Phi_{eq} = 0.4 = \frac{2}{5}$; $V_0 = 100$, $C_0 = 0.01$, $C = 0.02$.

Φ	E , mV
0.39600	-0.374
0.39800	-0.365
0.39960	-0.345
0.39980	-0.336
0.39996	-0.315
0.40000	-0.207
0.40004	1.322
0.40020	1.363
0.40040	1.381
0.40400	1.442

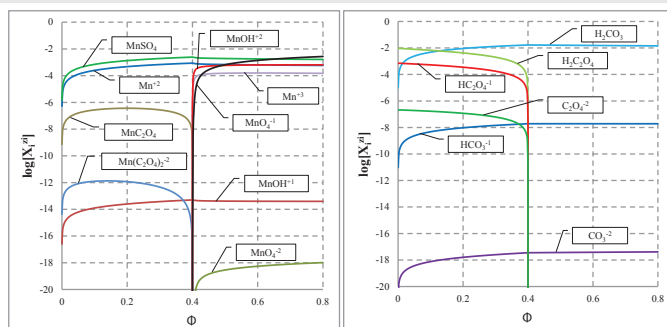


Figure 12: System III-3a: The speciation curves plotted for (12a) Fe and (12b) C (carbonate, oxalate) species at $V_0 = 100$, $C = 0.02$, $C_{01} = C_{02} = 0.02$, $C_{03} = 0.5$, $C_1 = C_{04} = 0$.

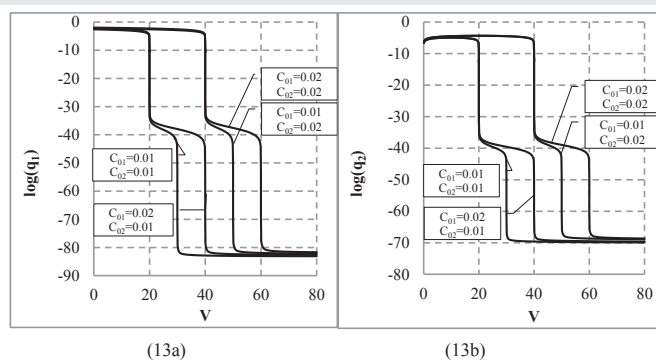


Figure 13: System IV: The $\log(q_i)$ vs. V relationships (Equations 54) plotted for (13a) Fe and (13b) Mn oxalates.

individual analytes: $FeSO_4$ (Figures 5a, 7a; Table 2) and $H_2C_2O_4$ (Figure 11a; Table 4) titrated with $KMnO_4$ solution (Table 1, system III-3a). The pH vs. Φ relationships are presented in Figures 5b, 11b, whereas the speciation curves are plotted in Figures 6a,b and 12a,b, resp.

To check the possibility of formation of the precipitates: FeC_2O_4 and MnC_2O_4 , the relationships: $\log q_1$ vs. V and $\log q_2$ vs. V were plotted (Figures 13a,b), where:

$$q_1 = \frac{[Fe^{+2}][C_2O_4^{-2}]}{K_{so1}}; q_2 = \frac{[Mn^{+2}][C_2O_4^{-2}]}{K_{so2}} \quad (54)$$

When $\log(q_i) < 0$ ($i = 1, 2$) (as in the case considered here), the products $[Fe^{+2}][C_2O_4^{-2}]$ and $[Mn^{+2}][C_2O_4^{-2}]$ do not attain the related K_{soi} values, i.e., the precipitates FeC_2O_4 and MnC_2O_4 are not formed here as equilibrium solid phases, i.e., and the relationships (46) are not valid. Then we have $a_1 = a_2 = 0$ in

Equations 50–52, at the pre-assumed data.

System IV

Balancing the system

V_0 mL of titrand D composed of KI (N_{03}) + H_2SO_4 (N_{04}) + H_2O (N_{05}) is titrated with V mL of $K_2Cr_2O_7$ (N_{01}) + H_2O (N_{02}) as titrant T added up to a defined point of the titration. In V_0+V mL of D+T mixture we have the following species:

H_2O (N_1), H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3), K^{+1} (N_4, n_4), HSO_4^{-1} (N_5, n_5), SO_4^{-2} (N_6, n_6), I^{-1} (N_7, n_7), I_3^{-1} (N_8, n_8),

I_2 (N_9, n_9), $I_{2(s)}$ (N_{10}, n_{10}), HIO (N_{11}, n_{11}), IO^{-1} (N_{12}, n_{12}), HIO_3 (N_{13}, n_{13}), IO_3^{-1} (N_{14}, n_{14}), H_5IO_6 (N_{15}, n_{15}),

$H_4IO_6^{-1}$ (N_{16}, n_{16}), $H_3IO_6^{-2}$ (N_{17}, n_{17}), $HCr_2O_7^{-1}$ (N_{18}, n_{18}), $Cr_2O_7^{-2}$ (N_{19}, n_{19}), H_2CrO_4 (N_{20}, n_{20}),

$HCrO_4^{-1}$ (N_{21}, n_{21}), CrO_4^{-2} (N_{22}, n_{22}), Cr^{+3} (N_{23}, n_{23}), $CrOH^{+2}$ (N_{24}, n_{24}), $Cr(OH)_2^{+1}$ (N_{25}, n_{25}),

$Cr(OH)_4^{-1}$ (N_{26}, n_{26}), $CrSO_4^{+1}$ (N_{27}, n_{27}).

On this basis, we formulate $f_1 = f(H)$, $f_2 = f(O)$ and then:

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

$$-N_2 + N_3 + 7N_5 + 8N_6 + N_{11} + 2N_{12} + 5N_{13} + 6N_{14} + 7N_{15} + 8N_{16} + 9N_{17} + 13N_{18} + 14N_{19} +$$

$$6N_{20} + 7N_{21} + 8N_{22} + N_{24} + 2N_{25} + 4N_{26} + 8N_{27} = 14N_{01} + 6N_{04} \quad (55)$$

$$f_0 = ChB$$

$$N_2 - N_3 + N_4 - N_5 - 2N_6 - N_7 - N_8 - N_{12} - N_{14} - N_{16} - 2N_{17} - N_{18} - 2N_{19} - N_{21} - 2N_{22} + 3N_{23} +$$

$$2N_{24} + N_{25} - N_{26} + N_{27} = 0 \quad (56)$$

$$f_3 = f(K) :$$

$$N_4 = 2N_{01} + N_{03} \quad (57)$$

$$f_4 = f(S) = f(SO_4) :$$

$$N_5 + N_6 + N_{27} = N_{04} \quad (58)$$

$$2 \cdot f(O) - f(H) + ChB - f(K) - 6 \cdot f(S) = 0 \Rightarrow \quad (59)$$

$$-N_7 - N_8 + N_{11} + N_{12} + 5N_{13} + 5N_{14} + 7N_{15} + 7N_{16} + 7N_{17} + 12N_{18} + 12N_{19} + 6N_{20} + 6N_{21} + 6N_{22} + 3N_{23} + 3N_{24} + 3N_{25} + 3N_{26} + 3N_{27} = 12N_{01} - N_{03} \quad \Rightarrow \quad (59a)$$

$$(-1) \cdot N_7 + (-1/3) \cdot 3N_8 + 0 \cdot (N_9 + N_{10}) + (+1) \cdot (N_{11} + N_{12}) +$$

$$(+5) \cdot (N_{13} + N_{14}) + (+7) \cdot (N_{15} + N_{16} + N_{17}) + (+6) \cdot (2N_{18} + 2N_{19} +$$

$$N_{20} + N_{21} + N_{22}) + (+3) \cdot (N_{23} + N_{24} + N_{25} + N_{26} + N_{27})$$

$$= (+6) \cdot 2N_{01} + (-1) \cdot N_{03} \quad \Rightarrow \quad (59b)$$

$$(-1) \cdot [I^{-1}] + (-1/3) \cdot 3[I_3^{-1}] + 0 \cdot (2[I_2] + 2[I_{2(s)}]) +$$

$$(+1) \cdot ([HIO] + [IO^{-1}]) + (+5) \cdot ([HIO_3] + [IO_3^{-1}]) +$$

$$(+7) \cdot ([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) + (+6) \cdot (2[HCr_2O_7^{-1}] +$$

$$2[Cr_2O_7^{-2}] + [H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}]) +$$

$$(+3) \cdot ([Cr^{+3}] + [CrOH^{+2}] + [Cr(OH)_2^{+1}] + [Cr(OH)_4^{-1}] +$$

$$[CrSO_4^{+1}]) = ((+6) \cdot 2CV + (-1) \cdot C_0V_0) / (V_0 + V) \quad (60)$$

where: $C_0V_0 = 10^3 \cdot N_{03} / N_A$, $CV = 10^3 \cdot N_{01} / N_A$. Note that Eq. 60 was obtained only from linear combination of electron-non-active elements (fans) in this system. The balances for electron-active elements (players) are as follows:

$$f_5 = f(I):$$

$$N_7 + 3N_8 + 2N_9 + 2N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + N_{15} +$$

$$N_{16} + N_{17} = N_{03} \quad (61)$$

$$[I^{-1}] + 3[I_3^{-1}] + 2 \cdot ([I_2] + [I_{2(s)}]) + ([HIO] + [IO^{-1}]) +$$

$$5 \cdot ([HIO_3] + [IO_3^{-1}]) + 7 \cdot ([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}])$$

$$= C_0V_0 / (V_0 + V) \quad (62)$$

$$f_6 = f(Cr):$$

$$2N_{18} + 2N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + N_{26} +$$

$$N_{27} = 2N_{01} \quad \Rightarrow \quad (63)$$

$$2[Cr_2O_7^{-2}] + [H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}] + [Cr^{+3}] +$$

$$[CrOH^{+2}] + [Cr(OH)_2^{+1}] + [Cr(OH)_4^{-1}] + [CrSO_4^{+1}]$$

$$= CV / (V_0 + V) \quad (64)$$

Subtraction of $3 \cdot f(Cr)$ (Eq. 63) from Eq. 59a and further operations give

$$[I^{-1}] + [I_3^{-1}] - ([HIO] + [IO^{-1}]) - 5 \cdot ([HIO_3] + [IO_3^{-1}]) -$$

$$7 \cdot ([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}])$$

$$- 3 \cdot (2[HCr_2O_7^{-1}] + 2[Cr_2O_7^{-2}] + [H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}])$$

$$= (C_0V_0 - 6CV) / (V_0 + V) \quad (65)$$

The simplest/shortest form of GEB, obtained from Equations 59, 61, 63, is the relation

$$2 \cdot f(O) - f(H) + ChB - f(K) - 6 \cdot f(S) + f(I) -$$

$$6 \cdot f(Cr) = 0 \quad \Rightarrow \quad (66)$$

$$N_8 + N_9 + N_{10} + N_{11} + N_{12} + 3 \cdot (N_{13} + N_{14}) + 4 \cdot (N_{15} + N_{16} + N_{17})$$

$$= 1.5 \cdot (N_{23} + N_{24} + N_{25} + N_{26}) \quad \Rightarrow \quad (66a)$$

$$[I_3^{-1}] + [I_2] + [I_{2(s)}] + [HIO] + [IO^{-1}] + 3 \cdot ([HIO_3] + [IO_3^{-1}]) +$$

$$4 \cdot ([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}])$$

$$= 1.5 \cdot ([Cr^{+3}] + [CrOH^{+2}] + [Cr(OH)_2^{+1}] + [Cr(OH)_4^{-1}] + [CrSO_4^{+1}]) \quad (66b)$$

Note that the numbers (N_{01} , N_{03}) of components forming the system are not involved in 66a.

Applying the atomic numbers: $Z_I = 53$ for I and $Z_{Cr} = 24$ for Cr, we obtain the linear combination

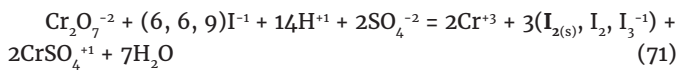
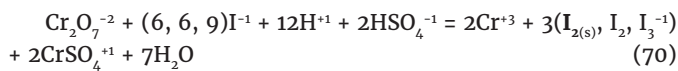
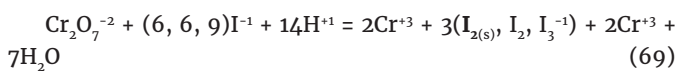
$$\begin{aligned} & Z_I \cdot f(I) + Z_{Cr} \cdot f(Cr) - (2 \cdot f(O) - f(H) + ChB \\ & - f(K) - 6 \cdot f(S)) = 0 \Rightarrow \\ & (Z_I + 1)N_7 + (3Z_I + 1)N_8 + 2Z_I(N_9 + N_{10}) + (Z_I - 1)(N_{11} + N_{12}) + \\ & (Z_I - 5)(N_{13} + N_{14}) + (Z_I - 7)(N_{15} + N_{16} + N_{17}) + (Z_{Cr} - 6)(2N_{18} + \\ & 2N_{19} + N_{20} + N_{21} + N_{22}) + (Z_{Cr} - 3)(N_{23} + N_{24} + N_{25} + N_{26}) \\ & = (Z_I + 1)N_{03} + 2(Z_{Cr} - 6)N_{01} \Rightarrow \quad (67) \\ & (Z_I + 1)[I^{-1}] + (3Z_I + 1)[I_3^{-1}] + 2Z_I([I_2] + [I_2]) + (Z_I - 1)([HIO] + [IO^{-1}]) \\ & + (Z_I - 5)([HIO_3] + [IO_3^{-1}]) + (Z_I - 7)([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) \\ & + (Z_{Cr} - 6)(2[HCr_2O_7^{-1}] + 2[Cr_2O_7^{-2}] + [H_2CrO_4] + [HCrO_4^{-1}] \\ & + [CrO_4^{-2}]) + (Z_{Cr} - 3)([Cr^{+3}] + [CrOH^{+2}] + [Cr(OH)_2^{+1}] + \\ & [Cr(OH)_4^{-1}] + [CrSO_4^{+1}]) \\ & = ((Z_I + 1) \cdot C_0 V_0 + 2(Z_{Cr} - 6) \cdot CV) / (V_0 + V) \quad (68) \end{aligned}$$

Equations: 60, 65, 66b, 68 (and other linear combinations, as well) are equivalent forms of GEB for this system. Eq. 68 is identical with the one obtained immediately on the basis of the Approach I to GEB [4].

Graphical presentation of results and discussion

The $E = E(\Phi)$ and $pH = pH(\Phi)$ and some speciation curves for iodine and chromium species are plotted in Figures 14a,b and 15a1,a2,b1,b2.

For $C_{01} = 0.01$, $I_{2(s)}$, $I_{2(s)}$ and I_3^{-1} are formed in reactions:



where the predominating products are involved. Binding the H^{+1} ions corresponds to the pH increase, which is the largest for low C_{01} value (relatively low buffer capacity of the solution).

At $C_{01} = 0.02$, $E = E(\Phi)$ and $[I_{2(s)}]$ pass through maximum at Φ ca. 0.2. The plot of $pH = pH(\Phi)$ shows a slight distortion of the course at $\Phi = 1/6$, and $DpH/D\Phi > 0$ for $\Phi > 0$. The $[IO_3^{-1}]$ is comparable with $[I_{2(s)}]$ and $[I_2]$; $[I_3^{-1}]$ is small here because $[I^{-1}] < 10^{-6}$. The reactions:

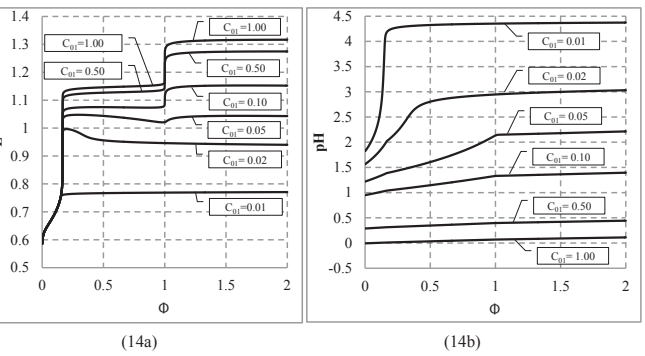


Figure 14: System IV: The plots $K_2Cr_2O_7 (C), V \Rightarrow KI (C_0) + H_2SO_4 (C_{01}), V_0$ system for (14a) $E = E(\Phi)$ and (14b) $pH = pH(\Phi)$, at $V_0 = 100, C_0 = 0.01$, and C_{01} values indicated at the corresponding curves.

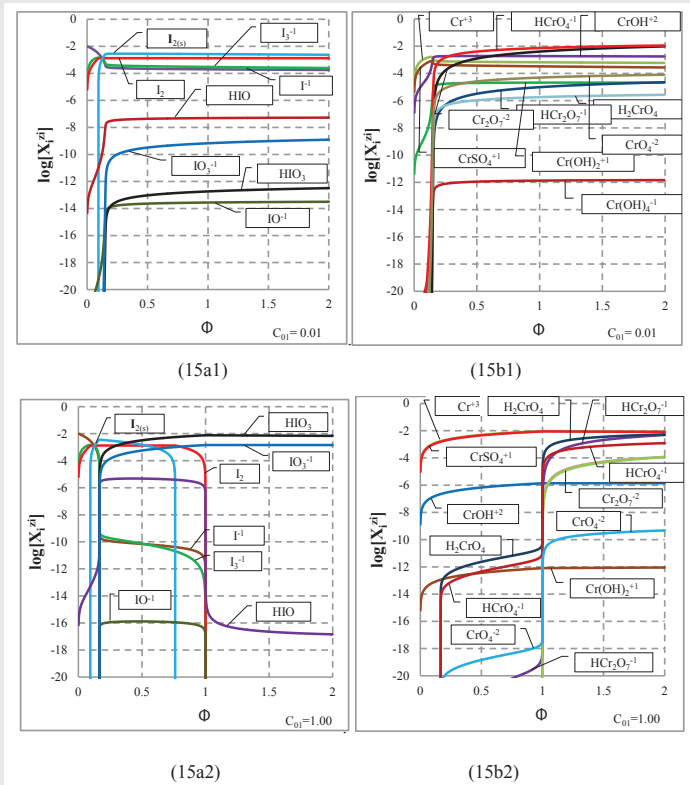
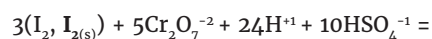
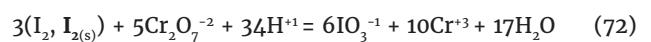
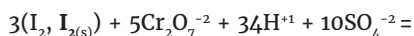
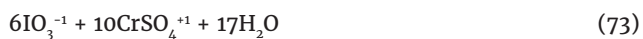


Figure 15: System IV: Speciation diagrams plotted for iodine (a1,a2) and chromium (b1,b2) species, at indicated C_{01} values.

Table 5: The pairs (Φ, E) in the vicinity of equivalence points at $C_{01} = 1.00$ mol/L H_2SO_4 .

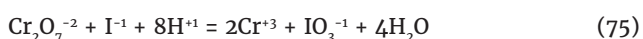
Φ	E, mV	Φ	E, mV
0.164	803.2	0.990	1158.6
0.165	815.7	0.995	1160.4
0.166	839.6	0.999	1164.6
1/6	1017.9	1.000	1197.6
0.167	1110.5	1.001	1270.6
0.168	1117.8	1.002	1276.5
0.169	1120.8	1.003	1279.9
0.170	1122.6	1.005	1284.2
...	...	1.010	1290.0





are clearly indicated.

At $C_{o1} = 0.05$, the function $E = E(\Phi)$ has a complex course; it first increases, reaches a maximum at $\Phi = 0.295$, then decreases, reaches a minimum at $\Phi = 1$, increases again, passes through a flat maximum at Φ ca. 1.6, and decreases. The curve $\text{pH} = \text{pH}(\Phi)$ breaks at $\Phi = 1/6$ and $\Phi = 1$. The $\text{I}_{2(s)}$ exists as the equilibrium solid phase at $0.0934 < \Phi < 0.762$. A decrease in $[\text{I}_2]$ value is more expressed at $\Phi > 1$. The ratio $[\text{HIO}_3]/[\text{IO}_3^{-1}]$ grows with growth of C_{o1} value. At $C_{o1} = 1.00$, the stoichiometry at $\Phi = \Phi_{\text{eq2}} = 1$ is described by the reaction



see Table 5.

At $C_{o1} \geq 0.1$, a jump on the $E = E(\Phi)$ curve at $\Phi = 1/6$ is clearly marked. The growth of jump at $\Phi = 1$ results from a more significant decrease in the $[\text{I}_2]$ value at $\Phi > 1$. The E-range covered by the jump at $\Phi = 1$ extends with an increase in the C_{o1} value (Figure 14a). For more details, see [4,14].

Computer program

```
function F = Function_K2Cr2O7_KI_H2SO4(x)
global Co C Co1 Vo V Vmin Vstep Vmax fi H OH pH E Kw
pKw A aa
global Cr3 CrOH CrOH2 CrOH4 CrSO4 Cr2O7 HCr2O7 CrO4
HCrO4 H2CrO4
global logCr3 logCrOH logCrOH2 logCrOH4 logCrSO4
logCr2O7 logHCr2O7
global logH2Cr2O7 logCrO4 logHCrO4 logH2CrO4
global I I3 I2 I2s HIO IO HI5O3 I5O3 H5I7O6 H4I7O6 H3I7O6
global logI logI3 logI2 logI2s logHIO logIO logHI5O3 logI5O3
logH5I7O6
global logH4I7O6 logH3I7O6
global SO4 HSO4 logSO4 logHSO4 K logK
E=x(1);
pH=x(2);
I=10.^-x(3);
SO4=10.^-x(4);
Cr3=10.^-x(5);
H=10.^-pH;
pKw=14;
Kw=10.^-14;
```

$$\text{OH}=\text{Kw}/\text{H};$$

$$\text{A}=16.9;$$

$$\text{ZI}=53;$$

$$\text{ZCr}=24;$$

$$\text{Cr2O7}=\text{Cr3}.\wedge 2.*10.\wedge (6.*\text{A}.*(E-1.33)+14.*\text{pH});$$

$$\text{HCr2O7}=10.\wedge 1.74.*\text{H}.*\text{Cr2O7};$$

$$\text{CrO4}=\text{Cr3}.*10.\wedge (3.*\text{A}.*(E-1.477)+8.*\text{pH});$$

$$\text{H2CrO4}=10.\wedge 7.27.*\text{H}.\wedge 2.*\text{CrO4};$$

$$\text{HCrO4}=10.\wedge 6.52.*\text{H}.*\text{CrO4};$$

$$\text{CrOH}=10.\wedge 10.1.*\text{Cr3}.*\text{OH};$$

$$\text{CrOH2}=10.\wedge 17.8.*\text{Cr3}.*\text{OH}.\wedge 2;$$

$$\text{CrOH4}=10.\wedge 29.9.*\text{Cr3}.*\text{OH}.\wedge 4;$$

$$\text{CrSO4}=10.\wedge 1.76.*\text{Cr3}.*\text{SO4};$$

$$\text{I2}=\text{I}.\wedge 2.*10.\wedge (2.*\text{A}.*(E-0.621));$$

$$\text{I3}=\text{I}.\wedge 3.*10.\wedge (2.*\text{A}.*(E-0.545));$$

$$\text{IO}=\text{I}.*10.\wedge (2.*\text{A}.*(E-0.49)+2.*\text{pH}-2.*\text{pKw});$$

$$\text{HIO}=\text{IO}.*10.\wedge (10.6-\text{pH});$$

$$\text{I5O3}=\text{I}.*10.\wedge (6.*\text{A}.*(E-1.08)+6.*\text{pH});$$

$$\text{HI5O3}=\text{I5O3}.*10.\wedge (0.79-\text{pH});$$

$$\text{H5I7O6}=\text{I}.*10.\wedge (8.*\text{A}.*(E-1.24)+7.*\text{pH});$$

$$\text{H4I7O6}=\text{H5I7O6}.*10.\wedge (-3.3+\text{pH});$$

$$\text{H3I7O6}=\text{I}.*10.\wedge (8.*\text{A}.*(E-0.37)+9.*\text{pH}-9.*\text{pKw});$$

$$\text{HSO4}=10.\wedge 1.8.*\text{H}.*\text{SO4};$$

$$\text{K}=(2.*\text{C}.*\text{V}+\text{Co}.*\text{Vo})./(\text{Vo}+\text{V});$$

if $\text{I2} > 1.33\text{e}-3$

$$\text{I2s}=\text{I2}-1.33\text{e}-3;$$

$$\text{I2}=1.33\text{e}-3;$$

$$\text{aa}=1;$$

else

$$\text{I2s}=0;$$

$$\text{aa}=0;$$

end;

%Concentration balance of I

$$\text{F}=[(\text{I}+3.*\text{I3}+2.*(\text{I2}+\text{aa}.*\text{I2s})+\text{H3I7O6}-\text{Co}.*\text{Vo})./(\text{Vo}+\text{V})];$$

%Concentration balance of S

$$(H_2SO_4 + SO_4 + CrSO_4 - C_{01} * V_0 / (V_0 + V));$$

%Concentration balance of Cr

$$(Cr_3 + CrOH + CrOH_2 + CrOH_4 + CrSO_4 + H_2CrO_4 + HCrO_4 + CrO_4 \dots$$

$$+ 2 * (HCr_2O_7 + Cr_2O_7) - 2 * C * V / (V_0 + V));$$

%Charge balance

$$(H - OH - I - I_3 - IO - I_5O_3 - H_4I_7O_6 -$$

$$2 * H_3I_7O_6 + 3 * Cr_3 + 2 * CrOH + CrOH_2 - CrOH_4 \dots$$

$$+ CrSO_4 - HCr_2O_7 - 2 * Cr_2O_7 - HCrO_4 - 2 * CrO_4 + K - 2 * SO_4 - HSO_4);$$

%Electron balance

$$((ZI + 1) * I + 2 * ZI * (I_2 + aa * I_2s) + (3 * ZI + 1) * I_3 \dots$$

$$+ (ZI - 1) * (HIO + IO) + (ZI - 5) * (HI_5O_3 + I_5O_3) \dots$$

$$+ (ZI - 7) * (H_5I_7O_6 + H_4I_7O_6 + H_3I_7O_6) \dots$$

$$+ (ZCr - 3) * (Cr_3 + CrOH + CrOH_2 + CrOH_4 + CrSO_4) + (ZCr - 6) * (H_2CrO_4 + HCrO_4 + CrO_4) \dots$$

$$+ 2 * (ZCr - 6) * (HCr_2O_7 + Cr_2O_7) \dots$$

$$- 2 * (ZCr - 6) * C * V / (V_0 + V) - (ZI + 1) * C_0 * V_0 / (V_0 + V));$$

$$\log I = \log_{10}(I);$$

$$\log I_2 = \log_{10}(I_2);$$

$$\log I_2s = \log_{10}(I_2s);$$

$$\log I_3 = \log_{10}(I_3);$$

$$\log HIO = \log_{10}(HIO);$$

$$\log IO = \log_{10}(IO);$$

$$\log HI_5O_3 = \log_{10}(HI_5O_3);$$

$$\log I_5O_3 = \log_{10}(I_5O_3);$$

$$\log H_5I_7O_6 = \log_{10}(H_5I_7O_6);$$

$$\log H_4I_7O_6 = \log_{10}(H_4I_7O_6);$$

$$\log H_3I_7O_6 = \log_{10}(H_3I_7O_6);$$

$$\log Cr_3 = \log_{10}(Cr_3);$$

$$\log CrOH = \log_{10}(CrOH);$$

$$\log CrOH_2 = \log_{10}(CrOH_2);$$

$$\log CrOH_4 = \log_{10}(CrOH_4);$$

$$\log CrSO_4 = \log_{10}(CrSO_4);$$

$$\log HCr_2O_7 = \log_{10}(HCr_2O_7);$$

$$\log Cr_2O_7 = \log_{10}(Cr_2O_7);$$

$$\log H_2CrO_4 = \log_{10}(H_2CrO_4);$$

$$\log HCrO_4 = \log_{10}(HCrO_4);$$

$$\log CrO_4 = \log_{10}(CrO_4);$$

$$\log HSO_4 = \log_{10}(HSO_4);$$

$$\log SO_4 = \log_{10}(SO_4);$$

$$\log K = \log_{10}(K);$$

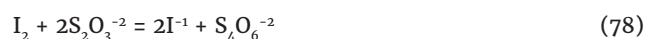
System V

Introducing remarks

This example is related to iodometric, indirect analysis of an acidified (H_2SO_4) solution of $CuSO_4$. On the preparatory step (stage 1° in Table 6), an excess of H_2SO_4 is neutralized with NH_3 until a blue colour of $Cu(NH_3)_i^{+2}$ complexes appears. Then CH_3COOH is added in an excess (stage 2°) to attain $pH \approx 3.5$. After the subsequent introduction of an excess of KI solution (stage 3°), the mixture with CuI precipitate and dissolved iodine formed in reactions:



is titrated with $Na_2S_2O_3$ solution (stage 4°), until the reduction of iodine:



is completed. At a due excess of KI, solid iodine ($I_{2(s)}$) does not precipitate.

More specifically, the analytical procedure/process in the system V consists of the following stages:

Stage 1°: addition of V mL of NH_3 (C_1) into V_0 mL $CuSO_4$ (C_0) + H_2SO_4 (C_{01});

Stage 2° : addition of V mL of CH_3COOH (C_2) into $V_0 + V_N$ mL $CuSO_4 + H_2SO_4 + NH_3$;

Stage 3°: addition of V mL of mol/L KI (C_3) into $V_0 + V_N + V_{Ac}$ mL $CuSO_4 + H_2SO_4 + NH_3 + CH_3COOH$;

Stage 4° : addition of V mL of mol/L $Na_2S_2O_3$ (C) into $V_0 + V_N + V_{Ac} + V_K$ mL $CuSO_4 + H_2SO_4 + NH_3 + CH_3COOH + KI$.

Table 6: Expressions for W in GEB and in concentration balances within the consecutive stages.

Stage	Solution added	W	V-range
1°	NH_3 (C_1)	$V_0 + V$	$(0, V_N >$
2°	CH_3COOH (C_2)	$V_0 + V_N + V$	$(0, V_{Ac} >$
3°	KI (C_3)	$V_0 + V_N + V_{Ac} + V$	$(0, V_K >$
4°	$Na_2S_2O_3$ (C)	$V_0 + V_N + V_{Ac} + V_K + V$	$(0, V_{max} >$

Volumes W of the D+T system at particular stages of the analytical procedure are presented in Table 6. At each stage, the variable V is considered as a volume of the solution added, consecutively: NH₃, CH₃COOH, KI and Na₂S₂O₃, although the true/factual titrant in this method is the Na₂S₂O₃ solution, added on the stage 4^o.

In this system, CuSO₄ (C₀) + H₂SO₄ (C₀₁) solution is considered as the sample tested; V_N is the total volume of NH₃ (C₁) added in the stage 1^o; V_{Ac} is the total volume of CH₃COOH (C₂) added in the stage 2^o, and V_K is the total volume of KI (C₃) added in the stage 3^o. The non-redox stages (1^o and 2^o) are then followed by the redox stages (3^o and 4^o).

The D+T system in the most complex stage 4^o of the procedure involves the following species:

H₂O (N₁), H⁺ (N₂, n₂), OH⁻ (N₃, n₃), K⁺ (N₄, n₄), Na⁺ (N₅, n₅), HSO₄⁻ (N₆, n₆), SO₄⁻² (N₇, n₇),

NH₄⁺ (N₈, n₈), NH₃ (N₉, n₉), CH₃COOH (N₁₀, n₁₀), CH₃COO⁻ (N₁₁, n₁₁), Cu²⁺ (N₁₂, n₁₂), CuOH⁺ (N₁₃, n₁₃), Cu(OH)₂ (N₁₄, n₁₄), Cu(OH)₃⁻ (N₁₅, n₁₅), Cu(OH)₄⁻² (N₁₆, n₁₆), CuSO₄ (N₁₇, n₁₇), CuNH₃⁺² (N₁₈, n₁₈),

Cu(NH₃)₂⁺² (N₁₉, n₁₉), Cu(NH₃)₃⁺² (N₂₀, n₂₀), Cu(NH₃)₄⁺² (N₂₁, n₂₁), CuCH₃COO⁺¹ (N₂₂, n₂₂),

Cu(CH₃COO)₂ (N₂₃, n₂₃), I⁻ (N₂₄, n₂₄), I₃⁻ (N₂₅, n₂₅), I₂ (N₂₆, n₂₆), I_{2(s)} (N₂₇, n₂₇), HIO (N₂₈, n₂₈),

IO⁻¹ (N₂₉, n₂₉), HIO₃ (N₃₀, n₃₀), IO₃⁻¹ (N₃₁, n₃₁), H₅IO₆ (N₃₂, n₃₂), H₄IO₆⁻¹ (N₃₃, n₃₃), H₃IO₆⁻² (N₃₄, n₃₄),

Cu⁺ (N₃₅, n₃₅), CuNH₃⁺¹ (N₃₆, n₃₆), Cu(NH₃)₂⁺¹ (N₃₇, n₃₇), CuI₂⁻¹ (N₃₈, n₃₈), CuI (N₃₉, n₃₉),

CuIO₃⁺¹ (N₄₀, n₄₀), H₂S₂O₃ (N₄₁, n₄₁), HS₂O₃⁻¹ (N₄₂, n₄₂), S₂O₃⁻² (N₄₃, n₄₃), S₄O₆⁻² (N₄₄, n₄₄),

CuS₂O₃⁻¹ (N₄₅, n₄₅), Cu(S₂O₃)₂⁻³ (N₄₆, n₄₆), Cu(S₂O₃)₃⁻⁵ (N₄₇, n₄₇). (80)

The numbers of components in the corresponding solutions are as follows: CuSO₄·5H₂O (N₀₁), H₂SO₄ (N₀₂), H₂O (N₀₃); NH₃ (N₀₄), H₂O (N₀₅); CH₃COOH (N₀₆), H₂O (N₀₇); KI (N₀₈), H₂O (N₀₉); Na₂S₂O₃·5H₂O (N₀₁₀), H₂O (N₀₁₁).

The equilibrium constants for the System V are involved in the relationships:

[H⁺] = 10^{-pH}, [OH⁻] = 10^{pH-14}, [NH₄⁺] = 10^{9.35}·[H⁺][NH₃], [HSO₄⁻] = 10^{1.8}·[H⁺][SO₄⁻²], [CH₃COOH] = 10^{4.65}·[H⁺][CH₃COO⁻], [CuOH⁺] = 10^{7.0}·[Cu²⁺][OH⁻], [Cu(OH)₂] = 10^{13.68}·[Cu²⁺][OH⁻]², [Cu(OH)₃⁻] = 10^{17.0}·[Cu²⁺][OH⁻]³, [Cu(OH)₄⁻²] = 10^{18.5}·[Cu²⁺][OH⁻]⁴, [CuNH₃⁺²] = 10^{3.39}·[Cu²⁺][NH₃], [Cu(NH₃)₂⁺²] = 10^{7.33}·[Cu²⁺][NH₃]², [Cu(NH₃)₃⁺²] = 10^{10.06}·[Cu²⁺][NH₃]³, [Cu(NH₃)₄⁺²] = 10^{12.03}·[Cu²⁺][NH₃]⁴, [CuSO₄] = 10^{2.36}·[Cu²⁺][SO₄⁻²],

[Cu⁺][I⁻] = 10^{-11.96} (solubility product for CuI), [CuI₂⁻¹] = 10^{8.85}·[Cu⁺][I⁻]², [CuIO₃⁺¹] = 10^{0.82}·[Cu²⁺][IO₃⁻¹], [CuCH₃COO⁺¹] =

10^{2.24}·[Cu²⁺][CH₃COO⁻¹], [Cu(CH₃COO)₂] = 10^{3.30}·[Cu²⁺][CH₃COO⁻¹]²,

[HS₂O₃⁻¹] = 10^{1.72}·[H⁺][S₂O₃⁻²], [H₂S₂O₃] = 10^{2.32}·[H⁺]²[S₂O₃⁻²],

[CuS₂O₃⁻¹] = 10^{10.3}·[Cu⁺][S₂O₃⁻²], [Cu(S₂O₃)₂⁻³] = 10^{12.2}·[Cu⁺][S₂O₃⁻²]², [Cu(S₂O₃)₃⁻⁵] = 10^{13.8}·[Cu⁺][S₂O₃⁻²]³, [HIO] = 10^{10.6}·[H⁺][IO₃⁻¹], [HIO₃] = 10^{0.79}·[H⁺][IO₃⁻¹] (81)

[Cu²⁺] = [Cu⁺]·10^{A(E-0.153)}}; [I₂] = [I⁻]²·10^{2A(E-0.621)}}, s = 1.33·10⁻³ mol/L (solubility of I_{2(s)}),

[I₃⁻] = [I⁻]³·10^{2A(E-0.545)}}, [IO⁻¹] = [I⁻]²·10^{2A(E-0.49)+2pH-28}}, [IO₃⁻¹] = [I⁻]²·10^{6A(E-1.08)+6pH}},

[H₅IO₆] = [I⁻]²·10^{8A(E-1.24)+7pH}}, [H₄IO₆⁻¹] = [H₅IO₆]²·10^{-3.3+pH}}, [H₃IO₆⁻²] = [I⁻]²·10^{8A(E-0.37)+9pH-126}}. (82)

In the calculations made here it was assumed that: V₀ = 100, C₀ = 0.01, C₀₁ = 0.01, C₁ = 0.25, C₂ = 0.75, C₃ = 2.0, C₄ = C = 0.1; V_N = 20, V_{Ac} = 40, V_K = 20.

In this system, three electron-active elements: Cu (Z_{Cu}=29), I (Z_I=53), S (Z_S=16) are involved.

Formulation of balances

For the (most complicated) stage 4^o, we have the following balances:

f₀ = ChB

N₂ - N₃ + N₄ + N₅ - N₆ - 2N₇ + N₈ - N₁₁ + 2N₁₂ + N₁₃ - N₁₅ - 2N₁₆ + 2N₁₈ + 2N₁₉ + 2N₂₀ + 2N₂₁ + N₂₂ - N₂₄ - N₂₅ - N₂₉ - N₃₁ - N₃₃ - 2N₃₄ + N₃₅ + N₃₆ + N₃₇ - N₃₈ + N₄₀ - N₄₂ - 2N₄₃ - 2N₄₄ - N₄₅ - 3N₄₆ - 5N₄₇ = 0 (83)

f₁ = f(H)

2N₁ + N₂(1+2n₂) + N₃(1+2n₃) + 2N₄n₄ + 2N₅n₅ + N₆(1+2n₆) + 2N₇n₇ + N₈(4+2n₈) + N₉(3+2n₉)

+ N₁₀(4+2n₁₀) + N₁₁(3+2n₁₁) + 2N₁₂n₁₂ + N₁₃(1+2n₁₃) + N₁₄(2+2n₁₄) + N₁₅(3+2n₁₅) + N₁₆(4+2n₁₆)

+ 2N₁₇n₁₇ + N₁₈(3+2n₁₈) + N₁₉(6+2n₁₉) + N₂₀(9+2n₂₀) + N₂₁(12+2n₂₁) + N₂₂(3+2n₂₂) + N₂₃(6+2n₂₃)

+ 2N₂₄n₂₄ + 2N₂₅n₂₅ + 2N₂₆n₂₆ + 2N₂₇n₂₇ + N₂₈(1+2n₂₈) + 2N₂₉n₂₉ + N₃₀(1+2n₃₀) + 2N₃₁n₃₁

+ N₃₂(5+2n₃₂) + N₃₃(4+2n₃₃) + N₃₄(3+2n₃₄) + 2N₃₅n₃₅ + N₃₆(3+2n₃₆) + N₃₇(6+2n₃₇) + 2N₃₈n₃₈

+ 2N₃₉n₃₉ + 2N₄₀n₄₀ + N₄₁(2+2n₄₁) + N₄₂(1+2n₄₂) + 2N₄₃n₄₃ + 2N₄₄n₄₄ + 2N₄₅n₄₅ + 2N₄₆n₄₆ + 2N₄₇n₄₇

= 10N₀₁ + 2N₀₂ + 2N₀₃ + 3N₀₄ + 2N₀₅ + 4N₀₆ + 2N₀₇ + 2N₀₉ + 10N₀₁₀ + 2N₀₁₁

f₂ = f(O)

N₁ + N₂n₂ + N₃(1+n₃) + N₄n₄ + N₅n₅ + N₆(4+n₆) + N₇(4+n₇) + N₈n₈ + N₉n₉ + N₁₀(2+n₁₀) + N₁₁(2+n₁₁) +

N₁₂n₁₂ + N₁₃(1+n₁₃) + N₁₄(2+n₁₄) + N₁₅(3+n₁₅) + N₁₆(4+n₁₆) +

$$N_{17}(4+n_{17}) + N_{18}n_{18} + N_{19}n_{19} + N_{20}n_{20} + N_{21}n_{21} + N_{22}(2+n_{22}) + N_{23}(4+n_{23}) + N_{24}n_{24} + N_{25}n_{25} + N_{26}n_{26} + N_{27}n_{27} + N_{28}(1+n_{28}) + N_{29}(1+n_{29}) +$$

$$N_{30}(3+n_{30}) + N_{31}(3+n_{31}) + N_{32}(6+n_{32}) + N_{33}(6+n_{33}) + N_{34}(6+n_{34}) + N_{35}n_{35} + N_{36}n_{36} + N_{37}n_{37} + N_{38}n_{38} +$$

$$N_{39}n_{39} + N_{40}(3+n_{40}) + N_{41}(3+n_{41}) + N_{42}(3+n_{42}) + N_{43}(3+n_{43}) + N_{44}(6+n_{44}) + N_{45}(3+n_{45}) + N_{46}(6+n_{46}) +$$

$$N_{47}(9+n_{47}) = 9N_{01} + 4N_{02} + N_{03} + N_{05} + 2N_{06} + N_{07} + N_{09} + 8N_{010} + N_{011}$$

$$-f_3 = -f(K)$$

$$N_{08} = N_4$$

$$-f_4 = -f(Na)$$

$$2N_{010} = N_5$$

$$-f_5 = -f(SO_4)$$

$$N_{01} + N_{02} = N_6 + N_7 + N_{17} \tag{84}$$

$$f_6 = f(NH_3)$$

$$N_8 + N_9 + N_{18} + N_{19} + N_{20} + 2N_{21} + N_{36} + 2N_{37} = N_{04} \tag{85}$$

$$f_7 = f(CH_3COO)$$

$$N_{10} + N_{11} + N_{22} + 2N_{23} = N_{06} \tag{86}$$

From the appropriate equations, we get their linear combinations:

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

$$-N_2 + N_3 + 7N_6 + 8N_7 - 4N_8 - 3N_9 + N_{11} + N_{13} + 2N_{14} + 3N_{15} + 4N_{16} + 8N_{17} - 3N_{18} - 6N_{19} - 9N_{20} - 12N_{21} +$$

$$N_{22} + 2N_{23} + N_{28} + 2N_{29} + 5N_{30} + 6N_{31} + 7N_{32} + 8N_{33} + 9N_{34} - 3N_{36} - 6N_{37} + 6N_{40} + 4N_{41} + 5N_{42} + 6N_{43} + 12N_{44} + 6N_{45} + 12N_{46} + 18N_{47} = 8N_{01} + 6N_{02} - 3N_{04} + 6N_{010} \tag{87}$$

$$2 \cdot f_2 - f_1 - f_3 - f_4 - 6f_5 + 3f_6$$

$$2N_{12} + 2N_{13} + 2N_{14} + 2N_{15} + 2N_{16} + 2N_{17} + 2N_{18} + 2N_{19} + 2N_{20} + 2N_{21} + 2N_{22} + 2N_{23} - N_{24} - N_{25}$$

$$+ N_{28} + N_{29} + 5N_{30} + 5N_{31} + 7N_{32} + 7N_{33} + 7N_{34} + N_{35} + N_{36} + N_{37} - N_{38} + 0 \cdot N_{39}$$

$$+ 7N_{40} + 4N_{41} + 4N_{42} + 4N_{43} + 10N_{44} + 5N_{45} + 9N_{46} + 13N_{47} = 2N_{01} + 4N_{010} - N_{08} \Rightarrow$$

$$(+2)(N_{12} + N_{13} + N_{14} + N_{15} + N_{16} + N_{17} + N_{18} + N_{19} + N_{20} + N_{21} + N_{22} + N_{23}) + (-1)N_{24} + 3 \cdot \left(-\frac{1}{3}\right) N_{25}$$

$$+ 2(0 \cdot N_{26} + 0 \cdot N_{27}) + (+1) \cdot (N_{28} + N_{29}) + (+5)(N_{30} + N_{31}) + (+7)(N_{32} + N_{33} + N_{34}) + (+1)(N_{35} + N_{36} + N_{37})$$

$$((+1)+2(-1))N_{38} + ((+1)+(-1)) \cdot N_{39} + ((+2)+(+5))N_{40} + 2(+2)(N_{41} + N_{42} + N_{43}) + 4 \cdot \left(+\frac{5}{2}\right) \cdot N_{44} + ((+1)+2(+2))N_{45} + ((+1)+2 \cdot 2(+2))N_{46} + ((+1)+3 \cdot 2(+2))N_{47} = (+2)N_{01} + (-1)N_{08} + 2(+2)N_{010} \Rightarrow \tag{88}$$

Assuming $W = V_0 + V_N + V_{Ac} + V_K + V$ (Table 6), from Eq. 88 we have:

$$2([Cu^{+2}] + [CuOH^{+1}] + [Cu(OH)_2] + [Cu(OH)_3^{-1}] + [Cu(OH)_4^{-2}] + [CuSO_4] + [CuNH_3^{+2}] + [Cu(NH_3)_2^{+2}] + [Cu(NH_3)_3^{+2}] + [Cu(NH_3)_4^{+2}] + [CuCH_3COO^{+1}] + [Cu(CH_3COO)_2] + ([Cu^{+1}] + [CuNH_3^{+1}] + [Cu(NH_3)_2^{+1}]) - [CuI_2^{-1}] + 7[CuIO_3^{+1}] - [I^{-1}] - [I_3^{-1}] + ([HIO] + [IO^{-1}]) + 5([HIO_3] + [IO_3^{-1}]) + 7([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) + 4([H_2S_2O_3] + [HS_2O_3^{-1}] + [S_2O_3^{-2}]) + 10[S_4O_6^{-2}] + 5[CuS_2O_3^{-1}] + 9[Cu(S_2O_3)_2^{-3}] + 13[Cu(S_2O_3)_3^{-5}] = (2C_0V_0 - C_3V_K + 4CV) \cdot \frac{1}{W} \tag{88a}$$

$$(+2)([Cu^{+2}] + [CuOH^{+1}] + [Cu(OH)_2] + [Cu(OH)_3^{-1}] + [Cu(OH)_4^{-2}] + [CuSO_4] + [CuNH_3^{+2}] + [Cu(NH_3)_2^{+2}] + [Cu(NH_3)_3^{+2}] + [Cu(NH_3)_4^{+2}] + [CuCH_3COO^{+1}] + [Cu(CH_3COO)_2] + (+1)([Cu^{+1}] + [CuNH_3^{+1}] + [Cu(NH_3)_2^{+1}]) + ((+1)+(-1)) \cdot [CuI] + ((+1)+2(-1))[CuI_2^{-1}] + ((+2)+(+5))[CuIO_3^{+1}] + (-1)[I^{-1}] + 3 \cdot \left(-\frac{1}{3}\right) \cdot [I_3^{-1}] + 2(0 \cdot [I_2] + 0 \cdot [I_{2(s)}]) + (+1) \cdot ([HIO] + [IO^{-1}]) + (+5)([HIO_3] + [IO_3^{-1}]) + (+7)([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) + 4([H_2S_2O_3] + [HS_2O_3^{-1}] + [S_2O_3^{-2}]) + 10[S_4O_6^{-2}] + 5[CuS_2O_3^{-1}] + 9[Cu(S_2O_3)_2^{-3}] + 13[Cu(S_2O_3)_3^{-5}] = ((+2)C_0V_0 + (-1)C_3V_K + 2(+2)CV) \cdot \frac{1}{W} \tag{88b}$$

where $W = V_0 + V_N + V_{Ac} + V_K + V$ for the stage 4°, see Table 6.

The ChB (Eq. 83) expressed in terms of concentrations is as follows:

where $W = V_0 + V_N + V_{Ac} + V_K + V$ for the stage 4°, see Table 6.

The ChB (Eq. 83) expressed in terms of concentrations is as follows:

$$[H^{+1}] - [OH^{-1}] + [K^{+1}] + [Na^{+1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] + [NH_4^{+1}] - [CH_3COO^{-1}] + 2[Cu^{+2}] + [CuOH^{+1}] - [Cu(OH)_3^{-1}] - 2[Cu(OH)_4^{-2}] + 2[CuNH_3^{+2}] + 2[Cu(NH_3)_2^{+2}] + 2[Cu(NH_3)_3^{+2}] + 2[Cu(NH_3)_4^{+2}] + [CuCH_3COO^{+1}] - [I^{-1}] - [I_3^{-1}] - [IO^{-1}] -$$

$$\begin{aligned}
 & [\text{IO}_3^{-1}] - [\text{H}_4\text{IO}_6^{-1}] - 2[\text{H}_3\text{IO}_6^{-2}] + [\text{Cu}^{+1}] + [\text{CuNH}_3^{+1}] + \\
 & [\text{Cu}(\text{NH}_3)_2^{+1}] - [\text{CuI}_2^{-1}] + [\text{CuIO}_3^{+1}] - [\text{HS}_2\text{O}_3^{-1}] - 2[\text{S}_2\text{O}_3^{-2}] - \\
 & 2[\text{S}_4\text{O}_6^{-2}] - [\text{CuS}_2\text{O}_3^{-1}] - 3[\text{Cu}(\text{S}_2\text{O}_3)_2^{-3}] - 5[\text{Cu}(\text{S}_2\text{O}_3)_3^{-5}] = 0 \quad (83a)
 \end{aligned}$$

The elemental/core balances are expressed in terms of equalities: $[\text{K}^{+1}] = C_3 \cdot \frac{V_k}{W}$, $[\text{Na}^{+1}] = 2C \cdot \frac{V}{W}$, and equations. For other electron-non-active elements (fans), we have:

$$[\text{HSO}_4^{-1}] + [\text{SO}_4^{-2}] + [\text{CuSO}_4^{-2}] - (C_0 + C_{01}) \cdot \frac{V_0}{W} = 0 \quad (84a)$$

$$\begin{aligned}
 & [\text{NH}_4^{+1}] + [\text{NH}_3] + [\text{CuNH}_3^{+2}] + 2[\text{Cu}(\text{NH}_3)_2^{+2}] + 3[\text{Cu}(\text{NH}_3)_3^{+2}] + \\
 & 4[\text{Cu}(\text{NH}_3)_4^{+2}] + [\text{CuNH}_3^{+1}] + 2[\text{Cu}(\text{NH}_3)_2^{+1}] - C_1 \cdot \frac{V_1}{W} = 0 \quad (85a)
 \end{aligned}$$

$$\begin{aligned}
 & [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^{-1}] + [\text{CuCH}_3\text{COO}^{+1}] + 2[\text{Cu}(\text{CH}_3\text{COO})_2] - \\
 & C_{Ac} \cdot \frac{V_A}{W} = 0 \quad (86a)
 \end{aligned}$$

The elemental and concentration balances for the electron-active elements ("players" [3]) are as follows:

$$f_8 = f(\text{Cu})$$

$$N_{12} + N_{13} + N_{14} + N_{15} + N_{16} + N_{17} + N_{18} + N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{35} + N_{36} + N_{37} + N_{38} + N_{38} +$$

$$N_{40} + N_{45} + N_{46} + N_{47} = N_{01} \Rightarrow \quad (89)$$

$$[\text{Cu}^{+2}] + [\text{CuOH}^{+1}] + [\text{Cu}(\text{OH})_2] + [\text{Cu}(\text{OH})_3^{-1}] + [\text{Cu}(\text{OH})_4^{-2}] + [\text{CuSO}_4] + [\text{CuNH}_3^{+2}] +$$

$$[\text{Cu}(\text{NH}_3)_2^{+2}] + [\text{Cu}(\text{NH}_3)_3^{+2}] + [\text{Cu}(\text{NH}_3)_4^{+2}] + [\text{CuCH}_3\text{COO}^{+1}] + [\text{Cu}(\text{CH}_3\text{COO})_2] +$$

$$[\text{Cu}^{+1}] + [\text{CuNH}_3^{+1}] + [\text{Cu}(\text{NH}_3)_2^{+1}] + [\text{CuI}_2^{-1}] + [\text{CuI}] + [\text{CuIO}_3^{+1}] + [\text{CuS}_2\text{O}_3^{-1}] +$$

$$\begin{aligned}
 & [\text{CuIO}_3^{+1}] + [\text{CuS}_2\text{O}_3^{-1}] + [\text{Cu}(\text{S}_2\text{O}_3)_2^{-3}] + \\
 & [\text{Cu}(\text{S}_2\text{O}_3)_3^{-5}] - C_0 \cdot \frac{V_0}{W} = 0 \quad (89a)
 \end{aligned}$$

$$f_9 = f(\text{I})$$

$$N_{24} + 3N_{25} + 2N_{26} + 2N_{27} + N_{28} + N_{29} + N_{30} + N_{31} + N_{32} + N_{33} + N_{34} + 2N_{38} + N_{39} + N_{40}$$

$$= N_{08} \Rightarrow \quad (90)$$

$$[\text{I}^{-1}] + 3[\text{I}_3^{-1}] + [\text{I}_2] + [\text{I}_{2(s)}] + [\text{HIO}] + [\text{IO}^{-1}] + [\text{HIO}_3] + [\text{IO}_3^{-1}] + [\text{H}_5\text{IO}_6] + [\text{H}_4\text{IO}_6^{-1}] + [\text{H}_3\text{IO}_6^{-1}] +$$

$$2[\text{CuI}_2^{-1}] + [\text{CuI}] + [\text{CuIO}_3^{+1}] - C_3 \cdot \frac{V}{W} = 0 \quad (90a)$$

$$f_{10} = f(\text{S})$$

$$2N_{41} + 2N_{42} + 2N_{43} + 4N_{44} + 2N_{45} + 4N_{46} + 6N_{47} = 2N_{010} \Rightarrow \quad (91)$$

$$N_{41} + N_{42} + N_{43} + 2N_{44} + N_{45} + 2N_{46} + 3N_{47} = N_{010} \Rightarrow$$

$$\begin{aligned}
 & [\text{H}_2\text{S}_2\text{O}_3] + [\text{HS}_2\text{O}_3^{-1}] + [\text{S}_2\text{O}_3^{-2}] + 2[\text{S}_4\text{O}_6^{-2}] + [\text{CuS}_2\text{O}_3^{-1}] + \\
 & 2[\text{Cu}(\text{S}_2\text{O}_3)_2^{-3}] + 3[\text{Cu}(\text{S}_2\text{O}_3)_3^{-5}] - C \cdot \frac{V}{W} = 0 \quad (91a)
 \end{aligned}$$

There is no symproportionation between sulphate, thiosulphate and tetrathionate species, i.e., sulphate species are in metastable state in this system. This is why sulphate species are formulated in separate core balance (Eq. 84a). Thiosulphate species are transformed into tetrathionate and then are involved together in Eq. 91a.

From the linear combination $Z_{Cu} \cdot f_8 + Z_1 \cdot f_9 + Z_S \cdot f_{10} - (f_{12} - f_3 - f_4 - 6f_5 + 3f_6)$, we formulate the balance

$$(Z_{Cu}-2)([\text{Cu}^{+2}] + [\text{CuOH}^{+1}] + [\text{Cu}(\text{OH})_2] + [\text{Cu}(\text{OH})_3^{-1}] + [\text{Cu}(\text{OH})_4^{-2}] + [\text{CuSO}_4] + [\text{CuNH}_3^{+2}] +$$

$$[\text{Cu}(\text{NH}_3)_2^{+2}] + [\text{Cu}(\text{NH}_3)_3^{+2}] + [\text{Cu}(\text{NH}_3)_4^{+2}] + [\text{CuCH}_3\text{COO}^{+1}] + [\text{Cu}(\text{CH}_3\text{COO})_2] +$$

$$(Z_{Cu}-1)([\text{Cu}^{+1}] + [\text{CuNH}_3^{+1}] + [\text{Cu}(\text{NH}_3)_2^{+1}]) + ((Z_{Cu}-1) + 2(Z_1+1))[\text{CuI}_2^{-1}] +$$

$$((Z_{Cu}-2) + (Z_1-5))[\text{CuIO}_3^{+1}] + (Z_1+1)[\text{I}^{-1}] + (3Z_1+1)[\text{I}_3^{-1}] + 2(Z_{Cu}-1+Z_1+1)([\text{I}_2] + a \cdot [\text{I}_{2(s)}]) +$$

$$(Z_1-1)([\text{HIO}] + [\text{IO}^{-1}]) + (Z_1-5)([\text{HIO}_3] + [\text{IO}_3^{-1}]) + (Z_1-7)([\text{H}_5\text{IO}_6] + [\text{H}_4\text{IO}_6^{-1}] + [\text{H}_3\text{IO}_6^{-2}]) +$$

$$2(Z_S-2)([\text{H}_2\text{S}_2\text{O}_3] + [\text{HS}_2\text{O}_3^{-1}] + [\text{S}_2\text{O}_3^{-2}]) + 4(Z_S-2.5)[\text{S}_4\text{O}_6^{-2}] + (Z_{Cu}-1+2(Z_S-2))[\text{CuS}_2\text{O}_3^{-1}] +$$

$$\begin{aligned}
 & (Z_{Cu}-1+4(Z_S-2))[\text{Cu}(\text{S}_2\text{O}_3)_2^{-3}] + (Z_{Cu}-1+6(Z_S-2))[\text{Cu}(\text{S}_2\text{O}_3)_3^{-5}] \\
 & - (Z_{Cu}-2)C_0V_0 + (Z_1+1)C_3V_K + 2(Z_{Cu}-2)CV \cdot \frac{1}{W} = 0 \quad (92)
 \end{aligned}$$

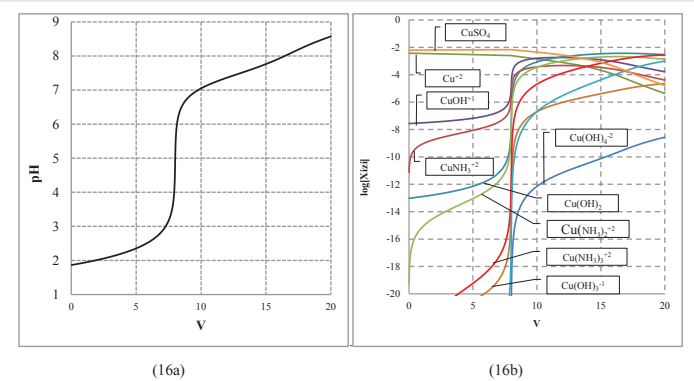


Figure 16: System V, stage 1°: (16a) pH vs. V curve, and (16b) speciation curves.

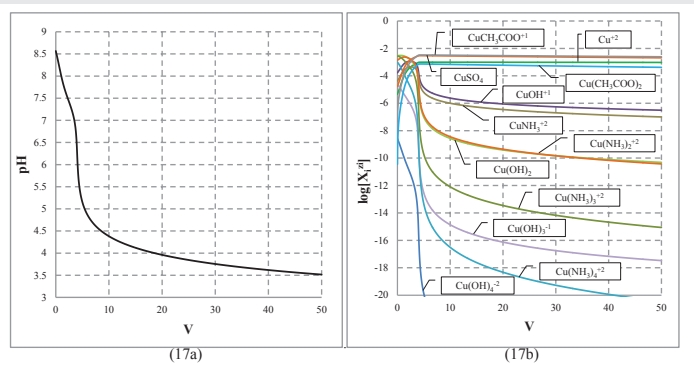


Figure 17: System V, stage 2°: plots of (17a) pH vs. V curve, and (17b) speciation curves.

where $W = V_0 + V_N + V_{Ac} + V_K + V$. It is the GEB identical with the one obtained according to Approach I to GEB. This confirms the equivalency of the Approaches I and II to GEB, also in this system.

Referring again to Eq. 87 which involves the balances for electron-non-active elements ("fans"), it should be noted that it does not involve $f_7 = f(\text{CH}_3\text{COO}) (= f(\text{C}))$, i.e., the balance with acetate species. Note that the formula for CH_3COOH can be rewritten as $\text{C}_2\text{H}_4\text{O}_2 = \text{C}_2(\text{H}_2\text{O})_2$. Taking the oxidation numbers: +1 and -2 for H and O resp., as coefficients at $f(\text{H})$ and $f(\text{O})$ found in Eq. 87, we calculate the oxidation number of C from the relation $2 \cdot x + 2 \cdot 0 = 0$, i.e., $x = 0$. For acetate ion, as CH_3COO^- and as a ligand in $\text{CuCH}_3\text{COO}^+$ and $\text{Cu}(\text{CH}_3\text{COO})_2$, we have $\text{C}_2(\text{H}_2\text{O})\text{OH}^-$ and then $2x + 0 + (-2+1) = -1$, i.e. $x = 0$ again. Then Eq. 87 can be rewritten as follows

$$2 \cdot f_2 - f_1 - f_3 - f_4 - 6f_5 + 3f_6 + 0 \cdot f_7 = 0 \Leftrightarrow$$

$$(+1) \cdot f(\text{H}) + (-2) \cdot f(\text{O}) + (+1) \cdot f(\text{K}) + (+1) \cdot f(\text{Na}) + (+6) \cdot f(\text{SO}_4) +$$

$$(-3) \cdot f(\text{NH}_3) + 0 \cdot f(\text{CH}_3\text{COO}) = 0 \quad (93)$$

Graphical presentation of results and discussion

To keep track of the gradual changes affected by addition of particular reagents in this system, it was assumed that all solutions of reagents (NH_3 , CH_3COOH , KI , $\text{Na}_2\text{S}_2\text{O}_3$) are added according to titrimetric mode.

At each stage, the variable V was considered as a volume of the solution added, consecutively: (1°) NH_3 (C_1), (2°) CH_3COOH (C_2), (3°) KI (C_3) and (4°) $\text{Na}_2\text{S}_2\text{O}_3$ (C) solutions, although – in principle – the true titrant T in this method is the $\text{Na}_2\text{S}_2\text{O}_3$ (C) solution. For stages 1° and 2°, the functions $\text{pH} = \text{pH}(V)$ and speciation curves are plotted in Figures 16a,b, 17a,b. For stages 3° and 4°, where redox reactions occur, the $E = E(V)$ and $\text{pH} = \text{pH}(V)$ functions are plotted together with the speciation curves, see Figures 18a-d, 19a,b and 20a-c. In stages 3° and 4°, the precipitate of CuI is formed. All stages (1° – 4°) are presented on the collected speciation diagram (Figure 22). The changes in the CuI solubility are illustrated by the dynamic solubility curves (Figures 23a,b).

Stage 1°

The pH-jump on the curve $\text{pH} = \text{pH}(V)$ (Figure 16a), corresponds to the stoichiometric point $\text{C}_1V_1 = 2\text{C}_{01}V_0$ of the titration where $V = V_1 \cong 8$ mL of NH_3 (C_1) is added into V_0 mL of H_2SO_4 (C_{01}) solution. An increase in the pH value is accompanied by growth in the concentrations of copper hydroxo- and ammonia-complexes, due to increases in the OH^- and NH_3 concentrations (Figure 16b). The titration was terminated at $V_N = 20$ mL, where pH ca. 8.5.

Stage 2°

The pH of the solution decreases (Figure 17a) as a result of the neutralization of an excess of NH_3 by CH_3COOH (C_2). The predominating copper species are in this case CuSO_4 , Cu^{+2} and $\text{CuCH}_3\text{COO}^+$ ($i=1,2$), Figure 17b. After addition of $V_{Ac} = 40$ mL of the acetic acid solution, the pH of the resulting solution is

ca. 3.5.

Stage 3°

The interesting course of the $E = E(V)$ curve is presented in Figure 18a. This curve initially decreases and reaches a "sharp" minimum at the point corresponding to crossing the solubility product for CuI . Precipitation of CuI starts after addition of 0.795 mL of 2.0 mol/L KI (Figure 18c). Subsequently, the curve increases, reaches a maximum and then decreases. At a due excess of the KI (C_3) added on the stage 3° ($V_K = 20$ mL), solid iodine ($\text{I}_{2(s)}$), of solubility 0.00133 mol/L at 25 °C) is not precipitated. Subsequently, the curve increases, reaches a maximum and then decreases. However, it should be noted that the E changes taking place within this stage are narrow, ca. 0.054 V (within 0.584 V at $V = 2.95$ mL and 0.530 V at $V =$

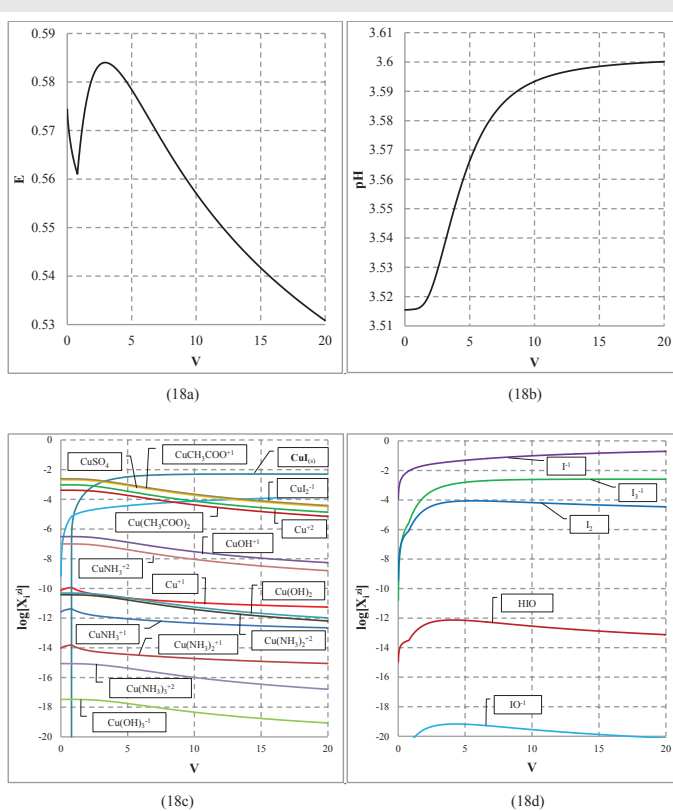


Figure 18: System V, stage 3°. Plots of (18a) $E = E(V)$ curve, (18b) $\text{pH} = \text{pH}(V)$ curve, and speciation curves: (18c) for Cu species, (18d) for iodine species.

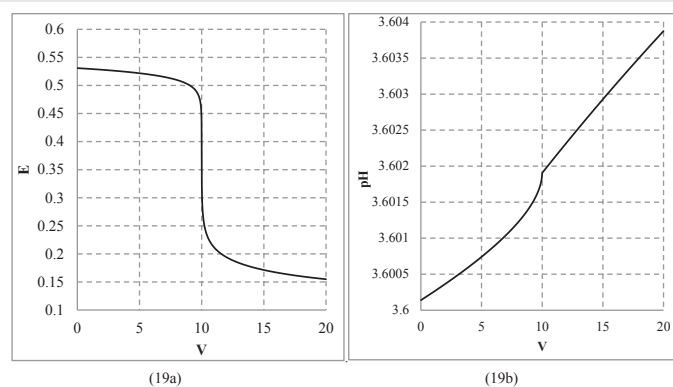


Figure 19: System V, stage 4°. Plots of (19a) E vs. V curve, (19b) pH vs. V curve.

20 mL), Figure 18a. The pH changes are equal to 0.085 pH unit, Figure 18b. In this stage, $V_K = 20$ mL of the KI ($C_3=2.0$) solution is added.

Precipitation of **CuI** (Equations 76, 77) starts after addition of 0.795 mL of 2.0 mol/L KI (Figure 18c). The concentration of CuI_2^{-1} increases with growth of $[I^{-1}]$ in the solution, and concentrations of $CuSO_4$, Cu^{+2} and $CuCH_3COO_i^{+2-i}$ ($i=1,2$) are still relatively high (Figure 18c). At high concentrations of I^{-1} (Figure 18d), $[I_2] < s = 1.33 \cdot 10^{-3}$ (solubility of $I_{2(s)}$ at 25°C) and then solid iodine is not formed in this system.

Stage 4°

The curve $E = E(V)$ in Figure 18a, related to the stage 3°, initially decreases and reaches a “sharp” minimum at the point corresponding to crossing the solubility product for **CuI** (Figure 18c).

The curve in Figure 19a shows a distinct jump (decrease) in potential E at the equivalence point ($V_{eq} = 10.0$ mL). A plot of the pH of V demonstrates a tiny break at this point (Figure 19b), virtually undetectable experimentally. At this stage, pH ranges from 3.5953 to 3.5956, within V -range $<0, 20>$; accuracy of pH measurements is not better than ± 0.001 pH unit. A marked decrease in the concentration of $Cu(+2)$ species occurs, whereas the concentration CuI_2^{-1} remains almost unchanged (Figure 20). The species I_3^{-1} and I_2 are consumed during the titration (Figure 21a). After crossing V_{eq} there is a significant increase in the concentrations of $Cu(S_2O_3)_i^{+1-2i}$ ($i=1,2,3$) species

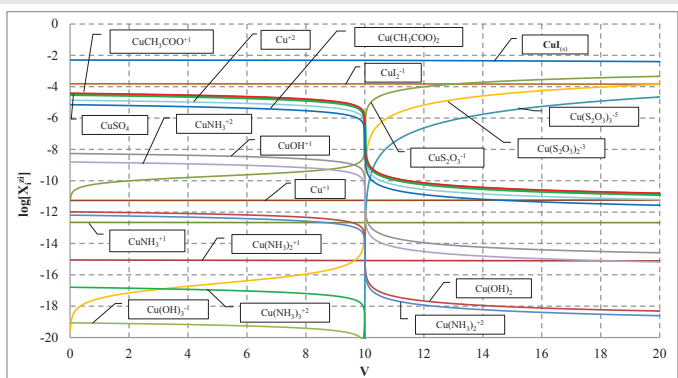


Figure 20: System V, stage 4°. The speciation curves plotted for Cu species.

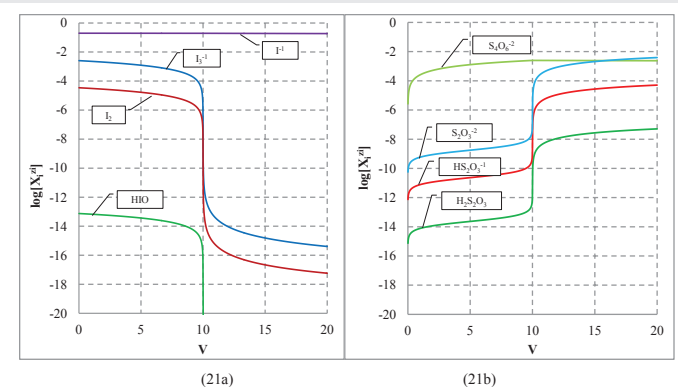


Figure 21: System V, stage 4°. The speciation curves for (21a) iodine species, (21b) tiosulphate and tetrasulphate species.

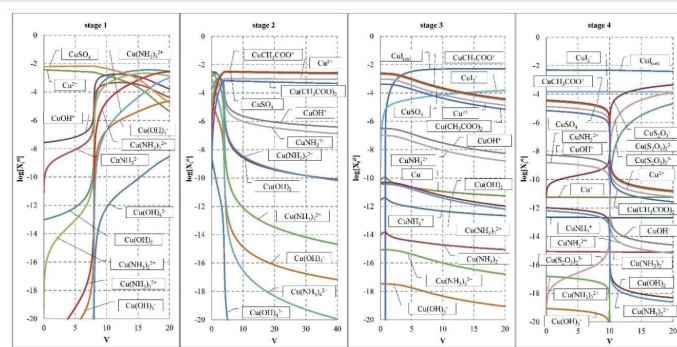


Figure 22: System V, stages 1° – 4°. The speciation plots for indicated Cu-species, within the successive stages. The V-values on the abscissas correspond to addition of V mL of: 0.25 mol/L NH_3 (stage 1°); 0.75 mol/L CH_3COOH (stage 2°); 2.0 mol/L KI (stage 3°); 0.1 mol/L $Na_2S_2O_3$ (stage 4°). For more details – see text.

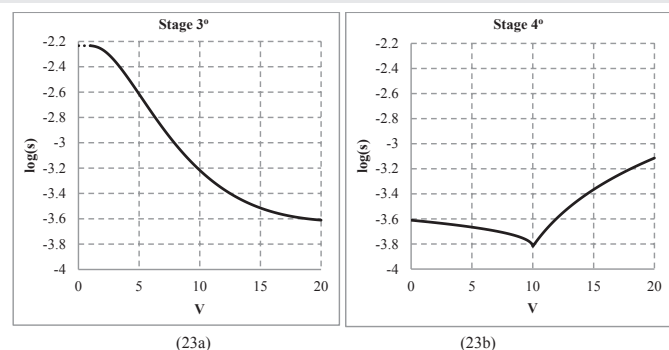


Figure 23: System V. Solubility s of **CuI** within: (23a) the stage 3°, (23b) the stage 4°.

(particularly $CuS_2O_3^{-1}$) (Figure 22). The plots for thiosulphate and tetrathionate species are presented in Figure 21b.

It is a very interesting system, both from analytical and physicochemical viewpoints. Because the standard potential $E_0 = 0.621$ V for (I_2, I^{-1}) exceeds $E_0 = 0.153$ V for (Cu^{+2}, Cu^{+1}), one could expect (at a first sight) the oxidation of Cu^{+1} by I_2 . However, such a reaction does not occur, due to the formation of sparingly soluble **CuI** precipitate ($pK_{so} = 11.96$).

The solubility s [mol/L] of **CuI** in this system is put in context with the speciation diagrams presented in Figure 22. This precipitate appears in the initial part of the titration with KI (C_3) solution (Figure 23a) and further it accompanies the titration, also in the stage 4° (Figure 23b). Within the stage 3°, at $V \geq 0.795$ mL, we have

$$s = s_3 = [Cu^{+2}] + \sum_{i=1}^4 [Cu(OH)_i^{+2-i}] + \sum_{i=1}^4 [Cu(NH_3)_i^{+2-i}] + [CuSO_4] + [CuIO_3^{+1}] + \sum_{i=1}^2 [Cu(CH_3COO)_i^{+2-i}] + [Cu^{+1}] + \sum_{i=1}^2 [Cu(NH_3)_i^{+1-i}] \quad (92)$$

and on the stage 4°

$$s = s_4 = s_3 + \sum_{i=1}^3 [Cu(S_2O_3)_i^{+1-i}] \quad (93)$$

The small concentration of Cu^{+1} (Figure 18c) occurs at a relatively high total concentration of $Cu(+2)$ species, determining the potential ca. 0.53 – 0.58 V, $[Cu^{+2}]/[Cu^{+1}] = 10^{A(E-0.153)}$, see Figure 18a. Therefore, the concentration of $Cu(+2)$ species determine a relatively high solubility s (Eq. 92)

in the initial part of stage 3°. The decrease in s value in further parts of the stage 3° is continued in the stage 4°, at $V < V_{eq} = C_0 V_0 / C = 0.01 \cdot 100 / 0.1 = 10$ mL (Figures 23a,b). Next, a growth in the solubility s_4 at $V > V_{eq}$ is involved with formation of thiosulfate complexes, mainly $CuS_2O_3^{-1}$ (Figure 20). The species I_3^{-1} and I_2 are consumed during the titration on the stage 4° (Figure 21a). A sharp drop of E value at $V_{eq} = 10$ mL (Eq.19a) corresponds to the fraction titrated $\Phi_{eq} = 1$.

Computer programs – Stages 1° – 4°

Stage 1°

function F = Stage_1_Cu_I_Function(x)

global C0 Ca C1 V0 V Vmin Vstep Vmax fi H OH pH Kw pKw A

global Cu2 CuOH CuOH2 CuOH3 CuOH4 Cu2NH3 Cu2NH32
Cu2NH33 Cu2NH34 CuSO4

global logCu2 logCuOH logCuOH2 logCuOH3 logCuOH4
logCu2NH3 logCu2NH32

global logCu2NH33 logCu2NH34 logCuSO4

global NH3 NH4 HSO4 SO4

global logNH3 logNH4 logHSO4 logSO4

pH=x(1);

Cu2=10.^(-x(2));

SO4=10.^(-x(3));

NH3=10.^(-x(4));

H=10.^(-pH);

pKw=14;

Kw=10.^(-14);

OH=Kw./H;

NH4=10.^9.35.*H.*NH3;

HSO4=10.^1.8.*H.*SO4;

CuSO4=10.^2.36.*Cu2.*SO4;

CuOH=10.^7.*Cu2.*OH;

CuOH2=10.^13.68.*Cu2.*OH.^2;

CuOH3=10.^17.*Cu2.*OH.^3;

CuOH4=10.^18.5.*Cu2.*OH.^4;

Cu2NH3=10.^3.39.*Cu2.*NH3;

Cu2NH32=10.^7.33.*Cu2.*NH3.^2;

Cu2NH33=10.^10.06.*Cu2.*NH3.^3;

Cu2NH34=10.^12.03.*Cu2.*NH3.^4;

%Concentration balance of Cu

F=[(Cu2+CuOH+CuOH2+CuOH3+CuOH4+CuSO4+Cu2NH3+
Cu2NH32+Cu2NH33+Cu2NH34...

-C0.*V0./(V0+V));

%Concentration balance of S

(HSO4+SO4+CuSO4-(C0+Ca).*V0./(V0+V));

%Concentration balance of ammonia

(NH3+NH4+Cu2NH3+2.*Cu2NH32+3.*Cu2NH33+4.*Cu2
NH34-C1.*V./(V0+V));

%Charge balance

(2.*Cu2+CuOH-CuOH3-2.*CuOH4-2.*SO4-

HSO4+2.*Cu2NH3+2.*Cu2NH32...

+2.*Cu2NH33+2.*Cu2NH34+H-OH+NH4)];

logCu2=log10(Cu2);

logCuOH=log10(CuOH);

logCuOH2=log10(CuOH2);

logCuOH3=log10(CuOH3);

logCuOH4=log10(CuOH4);

logCu2NH3=log10(Cu2NH3);

logCu2NH32=log10(Cu2NH32);

logCu2NH33=log10(Cu2NH33);

logCu2NH34=log10(Cu2NH34);

logCuSO4=log10(CuSO4);

logHSO4=log10(HSO4);

logSO4=log10(SO4);

logNH3=log10(NH3);

logNH4=log10(NH4);

Stage 2°

function F = Stage_2_Cu_I_Function(x)

global C0 Ca C1 C2 V0 VN V Vmin Vstep Vmax H OH pH Kw
pKw

global Cu2 CuOH CuOH2 CuOH3 CuOH4 Cu2NH3 Cu2NH32
Cu2NH33 Cu2NH34

global CuSO4 CuAc CuAc2

global logCu2 logCuOH logCuOH2 logCuOH3 logCuOH4
logCu2NH3 logCu2NH32

```
global logCu2NH33 logCu2NH34 logCuSO4 logCuAc
logCuAc2
```

```
global NH3 NH4 HSO4 SO4 Ac HAC
```

```
global logNH3 logNH4 logHSO4 logSO4 logAc logHAC
```

```
pH=x(1);
```

```
Cu2=10.^-x(2);
```

```
SO4=10.^-x(3);
```

```
NH3=10.^-x(4);
```

```
Ac=10.^-x(5);
```

```
H=10.^-pH;
```

```
pKw=14;
```

```
Kw=10.^-14;
```

```
OH=Kw./H;
```

```
NH4=10.^9.35.*H.*NH3;
```

```
HSO4=10.^1.8.*H.*SO4;
```

```
CuSO4=10.^2.36.*Cu2.*SO4;
```

```
CuOH=10.^7.*Cu2.*OH;
```

```
CuOH2=10.^13.68.*Cu2.*OH.^2;
```

```
CuOH3=10.^17.*Cu2.*OH.^3;
```

```
CuOH4=10.^18.5.*Cu2.*OH.^4;
```

```
Cu2NH3=10.^3.39.*Cu2.*NH3;
```

```
Cu2NH32=10.^7.33.*Cu2.*NH3.^2;
```

```
Cu2NH33=10.^10.06.*Cu2.*NH3.^3;
```

```
Cu2NH34=10.^12.03.*Cu2.*NH3.^4;
```

```
CuAc=10.^2.24.*Cu2.*Ac;
```

```
CuAc2=10.^3.30.*Cu2.*Ac.^2;
```

```
HAc=10.^4.65.*H.*Ac;
```

```
%Concentration balance of Cu
```

```
F=[(Cu2+CuOH+CuOH2+CuOH3+CuOH4+CuSO4+Cu2NH3+
Cu2NH32+Cu2NH33+Cu2NH34...
```

```
+CuAc+CuAc2-C0.*Vo./(Vo+VN+V));
```

```
%Concentration balance of sulfate
```

```
(HSO4+SO4+CuSO4-(C0+Ca).*Vo./(Vo+VN+V));
```

```
%Concentration balance of ammonia
```

```
(NH3+NH4+Cu2NH3+2.*Cu2NH32+3.*Cu2NH33+4.*Cu2
NH34...
```

```
-C1.*VN./(Vo+VN+V));
```

```
%Concentration balance of acetate
```

```
(Ac+HAc+CuAc+2.*CuAc2-C2.*V./(Vo+VN+V));
```

```
%Charge balance
```

```
(2.*Cu2+CuOH-CuOH3-2.*CuOH4-2*SO4-
```

```
HSO4+2.*Cu2NH3+2.*Cu2NH32...
```

```
+2.*Cu2NH33+2.*Cu2NH34+CuAc+H-OH-Ac+NH4)];
```

```
logCu2=log10(Cu2);
```

```
logCuOH=log10(CuOH);
```

```
logCuOH2=log10(CuOH2);
```

```
logCuOH3=log10(CuOH3);
```

```
logCuOH4=log10(CuOH4);
```

```
logCu2NH3=log10(Cu2NH3);
```

```
logCu2NH32=log10(Cu2NH32);
```

```
logCu2NH33=log10(Cu2NH33);
```

```
logCu2NH34=log10(Cu2NH34);
```

```
logCuSO4=log10(CuSO4);
```

```
logCuAc=log10(CuAc);
```

```
logCuAc2=log10(CuAc2);
```

```
logHSO4=log10(HSO4);
```

```
logSO4=log10(SO4);
```

```
logNH3=log10(NH3);
```

```
logNH4=log10(NH4);
```

```
logHAc=log10(HAc);
```

```
logAc=log10(Ac);
```

Stage 3°

```
function F = Stage_3_Cu_I_Function(x)
```

```
global C0 Ca C1 C2 C3 Vo VN VAc V Vmin Vstep Vmax fi H
OH pH E Kw pKw A
```

```
global I I3 I2 I2s HIO IO HI5O3 I5O3 H5I7O6 H4I7O6 H3I7O6
aa bb
```

```
global logI logI3 logI2 logI2s logHIO logIO logHI5O3 logI5O3
logH5I7O6
```

```
global Cu pr CuI2 CuNH3 CuNH32 logH4I7O6 logH3I7O6
```

```
global logCu logpr logCuI2 logCuNH3 logCuNH32
```

```
global Cu2 CuOH CuOH2 CuOH3 CuOH4 Cu2NH3 Cu2NH32
```

```

Cu2NH33 Cu2NH34
global CuSO4 CuIO3 CuAc CuAc2
global logCu2 logCuOH logCuOH2 logCuOH3 logCuOH4
logCu2NH3 logCu2NH32
global logCu2NH33 logCu2NH34 logCuSO4 logCuIO3
logCuAc logCuAc2
global NH3 NH4 HSO4 SO4 Ac HAc K
global logNH3 logNH4 logHSO4 logSO4 logAc logHAc logK
E=x(1);
pH=x(2);
I=10.^-x(3);
if bb==0;
Cu=10.^-x(4);
pr=0;
else
pr=10.^-x(4);
Cu=10.^-11.96./I;
end;
SO4=10.^-x(5);
NH3=10.^-x(6);Ac=10.^-x(7);
H=10.^-pH;
pKw=14;
Kw=10.^-14;
OH=Kw./H;
A=16.9;
ZI=53;
ZCu=29;
NH4=10.^9.35.*H.*NH3;
I2=I.^2.*10.^(2.*A.*(E-0.621));
I3=I.^3.*10.^(2.*A.*(E-0.545));
IO=I.*10.^(2.*A.*(E-0.49)+2.*pH-2.*pKw);
HIO=IO.*10.^(10.6-pH);
I5O3=I.*10.^(6.*A.*(E-1.08)+6.*pH);
HI5O3=I5O3.*10.^(0.79-pH);
H5I7O6=I.*10.^(8.*A.*(E-1.24)+7.*pH);

```

```

H4I7O6=H5I7O6.*10.^(-3.3+pH);
H3I7O6=I.*10.^(8.*A.*(E-0.37)+9.*pH-9.*pKw);
HSO4=(10.^1.8).*H.*SO4;
Cu2=10.^(A.*(E-0.153))*Cu;
CuSO4=10.^2.36.*Cu2.*SO4;
CuOH=10.^7.*Cu2.*OH;
CuOH2=10.^13.68.*Cu2.*OH.^2;
CuOH3=10.^17.*Cu2.*OH.^3;
CuOH4=10.^18.5.*Cu2.*OH.^4;
CuIO3=10.^0.82.*Cu2.*I5O3;
Cu2NH3=10.^3.39.*Cu2.*NH3;
Cu2NH32=10.^7.33.*Cu2.*NH3.^2;
Cu2NH33=10.^10.06.*Cu2.*NH3.^3;
Cu2NH34=10.^12.03.*Cu2.*NH3.^4;
CuI2=10.^8.85.*Cu.*I.^2;
CuNH3=10.^5.93.*Cu.*NH3;
CuNH32=10.^10.86.*Cu.*NH3.^2;
CuAc=10.^2.24.*Cu2.*Ac;
CuAc2=10.^3.30.*Cu2.*Ac.^2;
HAc=10.^4.65.*H.*Ac;
K=(C3.*V)/(V0+VN+VAc+V);
if I2>1.33e-3
I2s=I2-1.33e-3;
I2=1.33e-3;
aa=1;
else
I2s=0;
aa=0;
end;
%Concentration balance of Cu
F=[(bb.*pr+Cu+Cu2+CuOH+CuOH2+CuOH3+CuOH4+CuI2+
CuSO4+CuIO3...
+Cu2NH3+Cu2NH32+Cu2NH33+Cu2NH34+CuNH3+CuNH3
2+CuAc+CuAc2...
-Co.*V0)/(V0+VN+VAc+V)];

```

%Concentration balance of I

$$(bb \cdot pr + I + 3 \cdot I_3 + 2 \cdot (I_2 + aa \cdot I_2s) + HIO + IO + HI_5O_3 + I_5O_3 + H_5I_7O_6 \dots$$

$$+ H_4I_7O_6 + H_3I_7O_6 + 2 \cdot CuI_2 + CuIO_3 - C_3 \cdot V /$$

$$(V_0 + V_N + V_{Ac} + V);$$

%Concentration balance of sulfate

$$(HSO_4 + SO_4 + CuSO_4 - (Co + Ca) \cdot V_0 / (V_0 + V_N + V_{Ac} + V));$$

%Concentration balance of ammonia

$$(NH_3 + NH_4 + CuNH_3 + 2 \cdot CuNH_3_2 + Cu_2NH_3 + 2 \cdot Cu_2NH_3_2 + 3 \cdot Cu_2NH_3_3 \dots$$

$$+ 4 \cdot Cu_2NH_3_4 - C_1 \cdot V_N / (V_0 + V_N + V_{Ac} + V));$$

%Concentration balance of acetate

$$(Ac + HAc + CuAc + 2 \cdot CuAc_2 - C_2 \cdot V_{Ac} / (V_0 + V_N + V_{Ac} + V));$$

%Charge balance

$$(2 \cdot Cu_2 + Cu + CuOH - CuOH_3 - 2 \cdot CuOH_4 + CuIO_3 - CuI_2 - I - I_3 - IO - I_5O_3 - H_4I_7O_6 \dots$$

$$- 2 \cdot H_3I_7O_6 + 2 \cdot Cu_2NH_3 + 2 \cdot Cu_2NH_3_2 + 2 \cdot Cu_2NH_3_3 + 2 \cdot Cu_2NH_3_4 + CuNH_3 + CuNH_3_2 \dots$$

$$+ CuAc + H - OH + K - Ac + NH_4 - 2 \cdot SO_4 - HSO_4);$$

%Electron balance

$$((ZCu - 2) \cdot (Cu_2 + CuOH + CuOH_2 + CuOH_3 + CuOH_4 + Cu_2NH_3 + Cu_2NH_3_2 + Cu_2NH_3_3 \dots$$

$$+ Cu_2NH_3_4 + CuSO_4 + CuAc + CuAc_2) + (ZCu -$$

$$1) \cdot (Cu + CuNH_3 + CuNH_3_2) \dots$$

$$+ (ZCu + ZI - 7) \cdot CuIO_3 + (ZCu + ZI) \cdot bb \cdot pr + (ZCu + 2 \cdot ZI + 1) \cdot CuI_2 \dots$$

$$+ (ZI + 1) \cdot I + 2 \cdot ZI \cdot (I_2 + aa \cdot I_2s) + (3 \cdot ZI + 1) \cdot I_3 \dots$$

$$+ (ZI - 1) \cdot (HIO + IO) + (ZI - 5) \cdot (HI_5O_3 + I_5O_3) \dots$$

$$+ (ZI - 7) \cdot (H_5I_7O_6 + H_4I_7O_6 + H_3I_7O_6) \dots$$

$$- (ZCu - 2) \cdot Co \cdot V_0 / (V_0 + V_N + V_{Ac} + V) - (ZI + 1) \cdot C_3 \cdot V /$$

$$(V_0 + V_N + V_{Ac} + V)];$$

$$\log Cu = \log_{10}(Cu);$$

$$\log pr = \log_{10}(pr);$$

$$\log CuI_2 = \log_{10}(CuI_2);$$

$$\log CuNH_3 = \log_{10}(CuNH_3);$$

$$\log CuNH_3_2 = \log_{10}(CuNH_3_2);$$

$$\log Cu_2 = \log_{10}(Cu_2);$$

$$\log CuOH = \log_{10}(CuOH);$$

$$\log CuOH_2 = \log_{10}(CuOH_2);$$

$$\log CuOH_3 = \log_{10}(CuOH_3);$$

$$\log CuOH_4 = \log_{10}(CuOH_4);$$

$$\log Cu_2NH_3 = \log_{10}(Cu_2NH_3);$$

$$\log Cu_2NH_3_2 = \log_{10}(Cu_2NH_3_2);$$

$$\log Cu_2NH_3_3 = \log_{10}(Cu_2NH_3_3);$$

$$\log Cu_2NH_3_4 = \log_{10}(Cu_2NH_3_4);$$

$$\log CuSO_4 = \log_{10}(CuSO_4);$$

$$\log CuIO_3 = \log_{10}(CuIO_3);$$

$$\log CuAc = \log_{10}(CuAc);$$

$$\log CuAc_2 = \log_{10}(CuAc_2);$$

$$\log I = \log_{10}(I);$$

$$\log I_3 = \log_{10}(I_3);$$

$$\log I_2 = \log_{10}(I_2);$$

$$\log I_2s = \log_{10}(I_2s);$$

$$\log HIO = \log_{10}(HIO);$$

$$\log IO = \log_{10}(IO);$$

$$\log HI_5O_3 = \log_{10}(HI_5O_3);$$

$$\log I_5O_3 = \log_{10}(I_5O_3);$$

$$\log H_5I_7O_6 = \log_{10}(H_5I_7O_6);$$

$$\log H_4I_7O_6 = \log_{10}(H_4I_7O_6);$$

$$\log H_3I_7O_6 = \log_{10}(H_3I_7O_6);$$

$$\log HSO_4 = \log_{10}(HSO_4);$$

$$\log SO_4 = \log_{10}(SO_4);$$

$$\log NH_3 = \log_{10}(NH_3);$$

$$\log NH_4 = \log_{10}(NH_4);$$

$$\log HAc = \log_{10}(HAc);$$

$$\log Ac = \log_{10}(Ac);$$

$$\log K = \log_{10}(K);$$

Stage 4°

function F = Stage_4_Cu_I_Function(x)

global Co Ca C1 C2 C3 C V0 VN VAc VKI V Vmin Vstep Vmax
H OH pH

```

global E Kw pKw A aa bb
global I I3 I2 I2s HIO IO HI5O3 I5O3 H5I7O6 H4I7O6 H3I7O6
global logI logI3 logI2 logI2s logHIO logIO logHI5O3 logI5O3
global logH5I7O6 logH4I7O6 logH3I7O6
global Cu pr CuI2 CuNH3 CuNH32 CuS2O3 CuS2O32 CuS2O33
global logCu logpr logCuI2 logCuNH3 logCuNH32 logCuS2O3
global logCuS2O32 logCuS2O33 Cu2NH34 CuSO4 CuIO3
CuAc CuAc2
global Cu2 CuOH CuOH2 CuOH3 CuOH4 Cu2NH3 Cu2NH32
Cu2NH33
global logCu2 logCuOH logCuOH2 logCuOH3 logCuOH4
logCu2NH3
global logCu2NH32 logCu2NH33 logCu2NH34 logCuSO4
logCuIO3 logCuAc
global NH3 NH4 HSO4 SO4 Ac HAc S4O6 S2O3 HS2O3
H2S2O3 K Na logCuAc2
global logNH3 logNH4 logHSO4 logSO4 logAc logHAc
logS4O6
global logS2O3 logHS2O3 logH2S2O3 logK logNa
E=x(1);
pH=x(2);
I=10.^-x(3);
if bb==0
pr=0;
Cu=10.^-x(4);
else
pr=10.^x(4);
Cu=10.^-11.96./I;
end;
SO4=10.^-x(5);
NH3=10.^-x(6);
Ac=10.^-x(7);
S4O6=10.^-x(8);
H=10.^-pH;
pKw=14;
Kw=10.^-14;
OH=Kw./H;

```

```

A=16.9;
ZI=53;
ZCu=29;
ZS=16;
NH4=10.^9.35.*H.*NH3;
I2=I.^2.*10.^(2.*A.*(E-0.621));
I3=I.^3.*10.^(2.*A.*(E-0.545));
IO=I.*10.^(2.*A.*(E-0.49)+2.*pH-2.*pKw);
HIO=IO.*10.^(10.6-pH);
I5O3=I.*10.^(6.*A.*(E-1.08)+6.*pH);
HI5O3=I5O3.*10.^(0.79-pH);
H5I7O6=I.*10.^(8.*A.*(E-1.24)+7.*pH);
H4I7O6=H5I7O6.*10.^(-3.3+pH);
H3I7O6=I.*10.^(8.*A.*(E-0.37)+9.*pH-9.*pKw);
HSO4=10.^1.8.*H.*SO4;
Cu2=10.^(A.*(E-0.153))*Cu;
CuSO4=10.^2.36.*Cu2.*SO4;
CuOH=10.^7.*Cu2.*OH;
CuOH2=10.^13.68.*Cu2.*OH.^2;
CuOH3=10.^17.*Cu2.*OH.^3;
CuOH4=10.^18.5.*Cu2.*OH.^4;
CuIO3=10.^0.82.*Cu2.*I5O3;
Cu2NH3=10.^3.39.*Cu2.*NH3;
Cu2NH32=10.^7.33.*Cu2.*NH3.^2;
Cu2NH33=10.^10.06.*Cu2.*NH3.^3;
Cu2NH34=10.^12.03.*Cu2.*NH3.^4;
CuI2=10.^8.85.*Cu.*I.^2;
CuNH3=10.^5.93.*Cu.*NH3;
CuNH32=10.^10.86.*Cu.*NH3.^2;
CuAc=10.^2.24.*Cu2.*Ac;
CuAc2=10.^3.30.*Cu2.*Ac.^2;
HAc=10.^4.65.*H.*Ac;
S2O3=sqrt(S4O6./10.^(2.*A.*(E-0.09)));
HS2O3=10.^1.72.*H.*S2O3;

```

```

H2S2O3=10.^2.32.*(H.^2).*S2O3;
CuS2O3=10.^10.3.*Cu.*S2O3;
CuS2O32=10.^12.2.*Cu.*S2O3.^2;
CuS2O33=10.^13.8.*Cu.*S2O3.^3;
K=C3.*VKI./((V0+VN+VAc+VKI+V));
Na=2.*C.*V./((V0+VN+VAc+VKI+V));
if I2>1.33e-3
  I2s=I2-1.33e-3;
  I2=1.33e-3;
  aa=1;
else
  I2s=0;
  aa=0;
end;
%Concentration balance of Cu
F=[(bb.*pr+Cu+Cu2+CuOH+CuOH2+CuOH3+CuOH4+CuI2+
CuSO4+CuIO3...
+Cu2NH3+Cu2NH32+Cu2NH33+Cu2NH34+CuNH3+CuNH3
2+CuAc+CuAc2...
+CuS2O3+CuS2O32+CuS2O33-Co.*Vo./
(V0+VN+VAc+VKI+V));
%Concentration balance of I
(bb.*pr+I+3.*I3+2.*(I2+aa.*I2s)+HIO+IO+HI5O3+I5O3+H
5I7O6...
+H4I7O6+H3I7O6+2.*CuI2+CuIO3-C3.*VKI./
(V0+VN+VAc+VKI+V));
%Concentration balance of sulfate
(HSO4+SO4+CuSO4-(Co+Ca).*Vo./((V0+VN+VAc+VKI+V));
%Concentration balance of ammonia
(NH3+NH4+CuNH3+2.*CuNH32+Cu2NH3+2.*Cu2NH32+3.
*Cu2NH33+4.*Cu2NH34...
-C1.*VN./((V0+VN+VAc+VKI+V));
%Concentration balance of acetate
(Ac+HAc+CuAc+2.*CuAc2-C2.*VAc./((V0+VN+VAc+VKI+V));
%Concentration balance of thiosulfate
(H2S2O3+HS2O3+S2O3+2.*S4O6+CuS2O3+2.*CuS2O32+3.

```

```

*CuS2O33...
-C.*V./((V0+VN+VAc+VKI+V));
%Charge balance
(2.*Cu2+Cu+CuOH-CuOH3-2.*CuOH4+CuIO3-CuI2-I-I3-
IO-I5O3-H4I7O6...
-2.*H3I7O6-2.*SO4-HSO4+2.*Cu2NH3+2.*Cu2NH32+2.*
Cu2NH33...
+2.*Cu2NH34+CuNH3+CuNH32+CuAc+H-OH+K-Ac+NH4-
HS2O3-2.*S2O3...
-2.*S4O6+Na-CuS2O3-3.*CuS2O32-5.*CuS2O33);
%Electron balance
((ZCu-2).*(Cu2+CuOH+CuOH2+CuOH3+CuOH4+CuSO4)+(
ZCu+ZI-7).*CuIO3...
+(ZCu+ZI).*bb.*pr+(ZCu-1).*Cu+(ZCu-
1+2.*(ZI+1)).*CuI2...
+(ZI+1).*I+2.*ZI.*(I2+aa.*I2s)+(3.*ZI+1).*I3+(ZI-
1).*(HI5O3+I5O3)+(ZI-
7).*(H5I7O6+H4I7O6+H3I7O6)...
+(ZCu-2).*(Cu2NH3+Cu2NH32+Cu2NH33+Cu2NH34+CuAc
+CuAc2)...
+(ZCu-1).*(CuNH3+CuNH32)+(ZCu-1+2.*(ZS-
2)).*CuS2O3...
+(ZCu-1+4.*(ZS-2)).*CuS2O32+(ZCu-1+6.*(ZS-
2)).*CuS2O33...
+2.*(ZS-2).*(H2S2O3+HS2O3+S2O3)+4.*(ZS-2.5).*S4O6...
-(ZCu-2).*Co.*Vo./((V0+VN+VAc+VKI+V)...
-(ZI+1).*C3.*VKI./((V0+VN+VAc+VKI+V)...
-2.*(ZS-2).*C.*V./((V0+VN+VAc+VKI+V)));
logCu=log10(Cu);
logpr=log10(pr);
logCuI2=log10(CuI2);
logCuNH3=log10(CuNH3);
logCuNH32=log10(CuNH32);
logCuS2O3=log10(CuS2O3);
logCuS2O32=log10(CuS2O32);
logCuS2O33=log10(CuS2O33);
logCu2=log10(Cu2);
logCuOH=log10(CuOH);

```


$\log\text{CuOH}_2 = \log_{10}(\text{CuOH}_2)$;
 $\log\text{CuOH}_3 = \log_{10}(\text{CuOH}_3)$;
 $\log\text{CuOH}_4 = \log_{10}(\text{CuOH}_4)$;
 $\log\text{Cu}_2\text{NH}_3 = \log_{10}(\text{Cu}_2\text{NH}_3)$;
 $\log\text{Cu}_2\text{NH}_3\text{2} = \log_{10}(\text{Cu}_2\text{NH}_3\text{2})$;
 $\log\text{Cu}_2\text{NH}_3\text{3} = \log_{10}(\text{Cu}_2\text{NH}_3\text{3})$;
 $\log\text{Cu}_2\text{NH}_3\text{4} = \log_{10}(\text{Cu}_2\text{NH}_3\text{4})$;
 $\log\text{CuSO}_4 = \log_{10}(\text{CuSO}_4)$;
 $\log\text{CuIO}_3 = \log_{10}(\text{CuIO}_3)$;
 $\log\text{CuAc} = \log_{10}(\text{CuAc})$;
 $\log\text{CuAc}_2 = \log_{10}(\text{CuAc}_2)$;
 $\log\text{I} = \log_{10}(\text{I})$;
 $\log\text{I}_3 = \log_{10}(\text{I}_3)$;
 $\log\text{I}_2 = \log_{10}(\text{I}_2)$;
 $\log\text{I}_2\text{s} = \log_{10}(\text{I}_2\text{s})$;
 $\log\text{HIO} = \log_{10}(\text{HIO})$;
 $\log\text{IO} = \log_{10}(\text{IO})$;
 $\log\text{HI}_5\text{O}_3 = \log_{10}(\text{HI}_5\text{O}_3)$;
 $\log\text{I}_5\text{O}_3 = \log_{10}(\text{I}_5\text{O}_3)$;
 $\log\text{H}_5\text{I}_7\text{O}_6 = \log_{10}(\text{H}_5\text{I}_7\text{O}_6)$;
 $\log\text{H}_4\text{I}_7\text{O}_6 = \log_{10}(\text{H}_4\text{I}_7\text{O}_6)$;
 $\log\text{H}_3\text{I}_7\text{O}_6 = \log_{10}(\text{H}_3\text{I}_7\text{O}_6)$;
 $\log\text{S}_4\text{O}_6 = \log_{10}(\text{S}_4\text{O}_6)$;
 $\log\text{H}_2\text{S}_2\text{O}_3 = \log_{10}(\text{H}_2\text{S}_2\text{O}_3)$;
 $\log\text{HS}_2\text{O}_3 = \log_{10}(\text{HS}_2\text{O}_3)$;
 $\log\text{S}_2\text{O}_3 = \log_{10}(\text{S}_2\text{O}_3)$;
 $\log\text{HSO}_4 = \log_{10}(\text{HSO}_4)$;
 $\log\text{SO}_4 = \log_{10}(\text{SO}_4)$;
 $\log\text{NH}_3 = \log_{10}(\text{NH}_3)$;
 $\log\text{NH}_4 = \log_{10}(\text{NH}_4)$;
 $\log\text{HAc} = \log_{10}(\text{HAc})$;
 $\log\text{Ac} = \log_{10}(\text{Ac})$;
 $\log\text{Na} = \log_{10}(\text{Na})$;
 $\log\text{K} = \log_{10}(\text{K})$;

Generalized Equivalence Mass (GEM)

The main task of a titration is the estimation of the equivalent volume, V_{eq} , corresponding to the volume V of T , where the fraction titrated (Eq. 1) assumes the value

$$\Phi_{\text{eq}} = \frac{C \cdot V_{\text{eq}}}{C_0 \cdot V_0} \quad (94)$$

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

$$C_0 \cdot V_0 = 10^3 \cdot \frac{m_A}{M_A} \quad (95)$$

where m_A [g] and M_A [g/mol] denote mass and molar mass of analyte (A), respectively. From Equations: 1 and 95, we get

$$m_A = 10^{-3} \cdot C \cdot M_A \cdot \frac{V}{\Phi} \quad (96)$$

The value of the fraction $\frac{V}{\Phi}$ in Eq. 96, obtained from Eq. 1,

$$\frac{V}{\Phi} = \frac{C_0 \cdot V_0}{C} \quad (97)$$

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

$$\frac{V}{\Phi} = \frac{V_e}{\Phi_e} = \frac{V_{\text{eq}}}{\Phi_{\text{eq}}} \quad (98)$$

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

$$\Phi_e = \frac{C \cdot V_e}{C_0 \cdot V_0} \quad (99)$$

is the Φ -value related to the end point. From Equations 96 and 98, one obtains:

$$(a) m_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_e} \text{ and } (b) m_A = 10^{-3} \cdot C \cdot V_{\text{eq}} \cdot \frac{M_A}{\Phi_{\text{eq}}} \quad (100)$$

This does not mean that we may choose between Equations 100a and 100b, to calculate m_A . Namely, Eq. 100a cannot be applied for the evaluation of m_A : V_e is known, but Φ_e unknown. Calculation of Φ_e needs prior knowledge of C_0 value; e.g., for the titration system $\text{NaOH} (C, V) \rightarrow \text{HCl} (C_0, V_0)$ we have [2]

$$\Phi_e = \frac{C}{C_0} \cdot \frac{C_0 - \alpha_e}{C + \alpha_e} \quad (101)$$

where: $\alpha = [\text{H}^+] - [\text{OH}^-] = 10^{-\text{pH}} - 10^{\text{pH}-14}$, and $\alpha_e = \alpha(\text{pH}_e)$. However, C_0 is unknown before the titration; otherwise, the titration would be purposeless. In visual titration, the pH_e value is known only approximately. Also Eq. 100b is useless: the 'round' Φ_{eq} value is known exactly, but V_{eq} is unknown; V_e (not V_{eq}) is determined in visual titrations.

Because the Equations: 100a and 100b appear to be useless, the third, approximate formula for m_A , has to be applied [19], namely:

$$m'_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_{eq}} \Rightarrow m'_A = 10^{-3} \cdot C \cdot V_e \cdot R_A^{eq} \quad (102)$$

where Φ_{eq} is put for Φ_e in Eq. 100a, and

$$R_A^{eq} = \frac{M_A}{\Phi_{eq}} \quad (103)$$

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

$$\delta = \frac{m'_A - m_A}{m_A} = \frac{m'_A}{m_A} - 1 = \frac{V_e}{V_{eq}} - 1 = \frac{\Phi_e}{\Phi_{eq}} - 1 \quad (104)$$

The Generalized Equivalence Mass (GEM) concept was formulated (1979) by Michałowski [4,8,10,11,46], as the counterproposal to earlier (1978) IUPAC decision [47], see also [48].

Modified Gran methods of V_{eq} determination

The principal idea of the Gran (I) [49,50] and Gran (II) [51,52] methods, referred to potentiometric titrations, denoted later as G(I) and G(II) (for brevity), is based on evaluation of equivalence volume (V_{eq}), after transformation of fragments of S-shaped titration curve into linear segments. These methods were widely exploited later by chemists-analysts.

The progress in application of the Gran methods for analytical purposes was not uniform when recalculated on the main areas of titrimetric analysis, i.e., acid-base, redox, complexation and precipitation titrations. The G(I) and G(II) methods were mainly devoted to acid-base titration, with special emphasis put on alkalinity. As refers to redox systems, only a few papers of other authors were issued hitherto; all them were based on primitive models resulting from stoichiometry of redox reactions, where only the species entering the redox reaction notation were involved, see e.g. [53]. The functional dependencies based on those assumptions, gave erroneous experimental results for V_{eq} , as were stated e.g. by authors of the works [54-56], and in author's papers [16-19,23].

A new approach to this issue was successfully introduced and fully implemented by Michałowski [16-19] on the basis of GATES/GEB. The formulas resulting from the new approach were named as the modifications of the Gran methods, although the genesis of these modifications and the resulting functional relationships are fundamentally different from those offered by G(I) and G(II) methods.

The original models proposed entirely by Michałowski, and tentatively named as modifications of the Gran methods [16-19], will be illustrated on three examples of redox titrations of acidified (H_2SO_4) solutions of (i) $FeSO_4$ or (ii) $FeSO_4 + Fe_2(SO_4)_3$ as titrand (D).

Introductory relations

The redox potential E of a chemical system is measured with use of an inert metal (usually: platinum) as the indicator electrode in conjunction with a reference/counter electrode to form a complete cell; the E value in the system involved with redox reaction



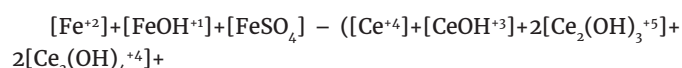
is expressed by the Nernst equation

$$E = E_0^* + \vartheta \cdot \log \frac{[Fe^{+3}]}{[Fe^{+2}]} \quad (106)$$

where ϑ is the real slope of indicator electrode, and E_0^* value is assumed constant during the titration.

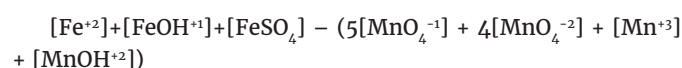
For further discussion, we collect the equations for GEB related to two different D+T systems: I-3 and II-3, with $FeSO_4$ (C_0) + H_2SO_4 (C_{01}) as the titrand D:

I-3 : for $Ce(SO_4)_2$ (C) + H_2SO_4 (C_1), $V \Rightarrow FeSO_4$ (C_0) + H_2SO_4 (C_{01}) system (System I-3) we have:



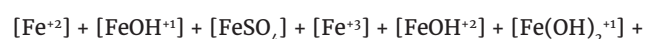
$$[CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}] = (C_0V_0 - CV)/(V_0 + V) \quad (25a)$$

II-3: for $KMnO_4$ (C), $V \Rightarrow FeSO_4$ (C_0) + H_2SO_4 (C_{01}) system (System II-3) we have:



$$= (C_0V_0 - 5CV)/(V_0 + V) \quad (42a)$$

In both systems (I-3 and II-3), the concentration balance for Fe is as follows:



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

From Equations 1 and 94, we have the relations: $CV = \Phi \cdot C_0V_0$, and $CV_{eq} = \Phi_{eq} \cdot C_0V_0$; then

$$\frac{V}{V_{eq}} = \frac{\Phi}{\Phi_{eq}} \quad (107)$$

At low pH values (Figures 3 and 5b), on the basis of speciation diagrams: Figures 4a,b (for the system I-3) and Figures 6a,b (for the system II-3), at $\Phi < \Phi_{eq}$ the balances: 42a, 25a and 18a can be presented in the simplified forms:

$$[Fe^{+2}] + [FeSO_4] = (C_0V_0 - CV)/(V_0 + V) \quad (\text{at } \Phi_{eq} < 1.0 \text{ for the system I-3}) \quad (25b)$$

$$[Fe^{+2}] + [FeSO_4] = (C_0V_0 - 5CV)/(V_0 + V) \quad (\text{at } \Phi_{eq} < 0.2 \text{ for the system II-3}) \quad (42b)$$

At $\Phi_{eq} < 1.0$ for the system I-3, and at $\Phi_{eq} < 0.2$ for the system II-3

$$[Fe^{+2}] + [FeSO_4] + [Fe^{+3}] + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}] = C_0V_0/(V_0 + V) \quad (18b)$$

Applying the relations:

$$[FeSO_4] = 10^{2.3}[Fe^{+2}][SO_4^{-2}]; [FeSO_4^{+1}] = 10^{4.18}[Fe^{+3}][SO_4^{-2}]; [Fe(SO_4)_2^{-1}] = 10^{7.4}[Fe^{+3}][SO_4^{-2}]^2$$

taken from (32), from Equations: 25b, 42b and 18b we get, by turns:

$$[\text{Fe}^{+2}] \cdot b_2 = (C_0 V_0 - CV)/(V_0 + V) \quad (108)$$

$$[\text{Fe}^{+2}] \cdot b_2 = (C_0 V_0 - 5CV)/(V_0 + V) \quad (109)$$

$$[\text{Fe}^{+2}] \cdot b_2 + [\text{Fe}^{+3}] \cdot b_3 = C_0 V_0 / (V_0 + V) \quad (110)$$

where :

$$b_2 = 1 + 10^{2.3} \cdot [\text{SO}_4^{-2}], \quad b_3 = 1 + 10^{4.18} \cdot [\text{SO}_4^{-2}] + 10^{7.4} \cdot [\text{SO}_4^{-2}]^2 \quad (111)$$

From Equations: 1, 107, 108, 110 and $\Phi_{\text{eq}} = 1$, we have

$$1 + \frac{b_3}{b_2} \cdot \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+2}]} = \frac{1}{1 - \Phi} \Rightarrow \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+2}]} = \frac{b_2}{b_3} \cdot \frac{\Phi}{1 - \Phi} = \frac{b_2}{b_3} \cdot \frac{V}{V_{\text{eq}} - V} \quad (112)$$

whereas from Equations: 1, 107, 109, 110 and $\Phi_{\text{eq}} = 0.2 \equiv \frac{1}{5}$, we have

$$\frac{b_3}{b_2} \cdot \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+2}]} = \frac{1}{1 - 5 \cdot \Phi} \Rightarrow \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+2}]} = \frac{b_2}{b_3} \cdot \frac{5 \cdot \Phi}{1 - 5 \cdot \Phi} = \frac{b_2}{b_3} \cdot \frac{V}{V_{\text{eq}} - V} \quad (113)$$

i.e., the expressions for the ratio $\frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+2}]}$ are identical in both systems. The values of this ratio depend on H_2SO_4 concentrations: C_{01} in D, and C_1 in T; we have $C_1 = 0$ in T for the System II-3. Then from Equations: 106 and 113 we get the equivalent relations [17]:

$$E = E_0^* - a \cdot \ln \frac{b_3}{b_2} + g \cdot \log V - g \cdot \log (V_{\text{eq}} - V) \quad (114)$$

$$E = E_0^* - a \cdot \ln \frac{b_3}{b_2} + a \cdot \ln V - a \cdot \ln (V_{\text{eq}} - V) \quad (115)$$

valid for $V < V_{\text{eq}}$, where

$$a = \frac{g}{\ln 10} \quad (116)$$

The relations $\ln \frac{b_3}{b_2}$ vs. Φ are plotted (I) for the systems: I-3 (Figure 24) and II-3 (Figure 25). Denoting $\theta = \ln \frac{b_3}{b_2}$, we see that $\frac{d\theta}{d\Phi} > 0$ in Figure 24 and $\frac{d\theta}{d\Phi} < 0$ in Figure 25. The θ vs. Φ relationships are quasi-linear, especially for greater C_{01} values.

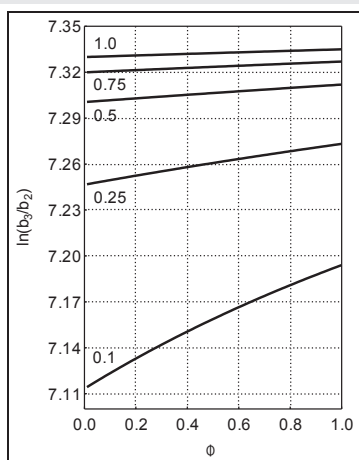


Figure 24: The $\ln \frac{b_3}{b_2}$ vs. Φ dependence for the system I-3 at $V_0 = 100$, $C_0 = 0.01$, $C = 0.1$, $C_1 = 0.5$, $C_{02} = C_2 = 0$ and various concentrations (C_{01}) of H_2SO_4 in D, indicated at the corresponding lines (see Table 1).

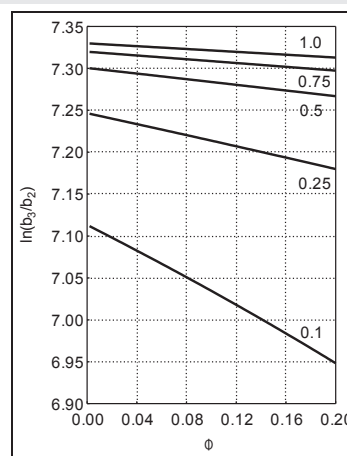


Figure 25: The $\ln \frac{b_3}{b_2}$ vs. Φ dependence for the system II-3 at $C_1 = 0$, $V_0 = 100$, $C_0 = 0.01$, $C = 0.02$, $C_{02} = C_1 = 0$ and various concentrations (C_{01}) of H_2SO_4 in D, indicated at the corresponding lines.

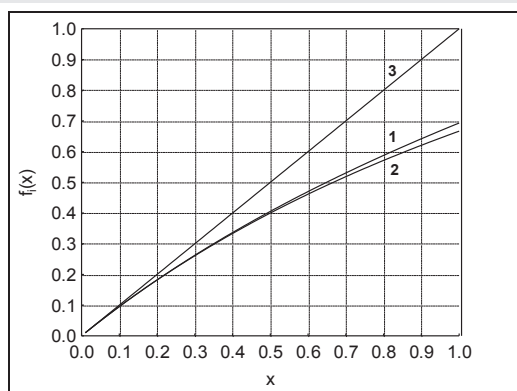


Figure 26: Comparison of the plots for: (1) $f_1(x) = \ln(1+x)$, (2) $f_2(x) = \left(\frac{1}{x} + \frac{1}{2}\right)^{-1}$ and (3) $f_3(x) = x$, $x \in < 0, 1 >$.

Then we can assume the relation

$$\ln \frac{b_3}{b_2} = \alpha - \gamma \cdot \Phi = \alpha - \beta \cdot V \quad (117)$$

where α , β and γ denote constant values for the given titration. Applying Eq. 116 in Eq. 115, we have

$$E = \omega + a \cdot \beta \cdot V + a \cdot \ln V - a \cdot \ln (V_{\text{eq}} - V) \quad (118)$$

where $\omega = E_0^* - a \cdot \alpha$ is the new constant value, obtained from constant values introduced above.

Formulation of the Gran methods

For two consecutive points (V_j, E_j) and (V_{j+1}, E_{j+1}) referred to potentiometric titration of D with T, from Eq. 118 we have

$$E_{j+1} - E_j = a \cdot \beta \cdot (V_{j+1} - V_j) + a \cdot \ln \frac{V_{j+1}}{V_j} - a \cdot \ln \frac{V_{\text{eq}} - V_{j+1}}{V_{\text{eq}} - V_j} \quad (119)$$

Applying in Eq. 119 the identities:

$$\frac{V_{j+1}}{V_j} = 1 + x_{1j}, \quad \frac{V_{\text{eq}} - V_{j+1}}{V_{\text{eq}} - V_j} = 1 - x_{2j}$$

where :

$$x_{1j} = \frac{V_{j+1} - V_j}{V_j}, x_{2j} = \frac{V_{j+1} - V_j}{V_{eq} - V_j} \quad (120)$$

we get

$$E_{j+1} - E_j = a \cdot \beta \cdot (V_{j+1} - V_j) + a \cdot \ln(1 + x_{1j}) - a \cdot \ln(1 - x_{2j}) \quad (121)$$

Applying the approximation [46,57] (see Figure 26)

$$\ln(1 \pm x_{ij}) \cong \pm \frac{x_{ij}}{1 \pm \frac{x_{ij}}{2}} = \pm \left(\frac{1}{x_{ij}} \pm \frac{1}{2} \right)^{-1} \quad (122)$$

we write

$$\ln(1 + x_{1j}) - \ln(1 - x_{2j}) = \left(\frac{1}{x_{1j}} + \frac{1}{2} \right)^{-1} + \left(\frac{1}{x_{2j}} - \frac{1}{2} \right)^{-1} \quad (123a)$$

$$= 4 \cdot \frac{x_{1j} + x_{2j}}{(2 + x_{1j})(2 - x_{2j})} = \frac{(V_{j+1} - V_j) \cdot V_{eq}}{V_j \cdot (V_{eq} - V_j)} = (V_{j+1} - V_j) \cdot \left(\frac{1}{V_j} + \frac{1}{V_{eq} - V_j} \right) \quad (123b)$$

where

$$V_j^* = \frac{V_j + V_{j+1}}{2} \quad (124)$$

Applying Eq. 123b in Eq. 121, we get

$$y_j = \frac{E_{j+1} - E_j}{V_{j+1} - V_j} = a \cdot \beta + a \cdot \left(\frac{1}{V_j^*} + \frac{1}{V_{eq} - V_j^*} \right) \quad (125)$$

At high C_{O_1} value, the change of $\ln \frac{b_3}{b_2}$ value in Eq. 117 is relatively small; $= 1.7 \cdot 10^{-3}$ at $C_{O_1} = 1$ mol/L. Then the assumption $\ln \frac{b_3}{b_2} = \text{const.}$ can be applied below in the simplified Gran models. For lower C_{O_1} values, this assumption provides a kind of drift introduced by the model applied; then in accurate models, Eq. 125 is used; the parameters: V_{eq} , a and β are obtained there according to an iterative computer program, by minimization of the sum of squares

$$SS = \sum_j \left(a \cdot \beta + a \cdot \left(\frac{1}{V_j^*} + \frac{1}{V_{eq} - V_j^*} \right) - y_j \right)^2 \quad (126)$$

Assuming $\ln \frac{b_3}{b_2} = \text{const.}$, i.e., setting $\beta = 0$ in Eq. 125, we get

$$y_j^* = \frac{1}{V_j^*} \cdot \frac{V_{j+1} - V_j}{E_{j+1} - E_j} = G_1 \cdot (V_{eq} - V_j^*) \quad (127)$$

where

$$G_1 = \frac{1}{a \cdot V_{eq}} \quad (128)$$

is a constant value, for the specific titration. Denoting

$$R = G_1 \cdot V_{eq} \quad (129)$$

from Eq. 127 we have the regression equation

$$y_j^* = R - G_1 \cdot V_j^* + \varepsilon_j \quad (130)$$

The R and G_1 are determined there according to least squares method:

$$R = \frac{\sum y_j^* \cdot \sum V_j^{*2} - \sum V_j^* \cdot \sum y_j^* V_j^*}{(N-1) \cdot \sum V_j^{*2} - (\sum V_j^*)^2}; G_1 = - \frac{(N-1) \cdot \sum y_j^* V_j^* - \sum y_j^* \cdot \sum V_j^*}{(N-1) \cdot \sum V_j^{*2} - (\sum V_j^*)^2}$$

and then

$$V_{eq} = \frac{R}{G_1} = \frac{\sum V_j^* \cdot \sum y_j^* V_j^* - \sum y_j^* \cdot \sum V_j^{*2}}{(N-1) \cdot \sum y_j^* V_j^* - \sum y_j^* \cdot \sum V_j^*} \quad (132)$$

where $\sum = \sum_{j=1}^{N-1}$ in Eq. 131, 132; N – number of exp. points (V_j, E_j) | $j=1, \dots, N$.

Other options are also possible. Applying relation 116, from Eq. 115 we have, by turns:

$$E_0^* - E = \theta \cdot \log \left(\frac{b_3}{b_2} \cdot \frac{V_{eq} - V}{V} \right) \quad (133)$$

$$V \cdot 10^{\frac{E}{\theta}} = 10^{\frac{E_0^*}{\theta}} \cdot \frac{b_3}{b_2} \cdot (V_{eq} - V) \quad (134)$$

Applying the approximation 117, we have

$$\frac{b_3}{b_2} = e^{\alpha} \cdot e^{-\beta \cdot V} \cong e^{\alpha} \cdot (1 - \beta \cdot V) \quad (135)$$

Inserting Eq. 135 into Eq. 134 and denoting $b = 10^{\frac{E_0^*}{\theta}} \cdot e^{\alpha}$, we get

$$V \cdot 10^{\frac{E}{\theta}} = b \cdot (1 - \beta \cdot V) \cdot (V_{eq} - V) = P \cdot V^2 - Q \cdot V + R \quad (136)$$

where:

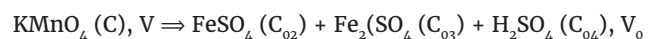
$$P = b \cdot \beta, Q = b \cdot (\beta \cdot V_{eq} + 1), R = b \cdot V_{eq} \quad (137)$$

The values for P, Q, R are then determined according to the least squares method. On the basis of Equations 137, we get, by turns,

$$\frac{R}{P} = \frac{V_{eq}}{\beta}, \frac{Q}{R} = \beta + \frac{1}{V_{eq}}, P \cdot V_{eq}^2 - Q \cdot V_{eq} + R = 0 \Rightarrow V_{eq} = \frac{Q - \sqrt{Q^2 - 4 \cdot P \cdot R}}{2 \cdot P} \quad (138)$$

Formulation of the system VI

Referring to the system VI (Table 1)



One can state that the composition of the titrand can be affected here by partial oxidation of the iron(II) species by oxygen from air.

From the balances we obtain the equation

$$[Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] - (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}]) = \frac{C_{O_2} \cdot V_0 - 5 \cdot C \cdot V}{V_0 + V} \quad (139)$$

As previously, at $\Phi < 0.2$, Eq. 139 simplifies to

$$[Fe^{+2}] \cdot b_2 = C_{O_2} V_0 \cdot \frac{1 - 5 \cdot \Phi}{V_0 + V}$$

and the concentration balance for Fe is transformed into the form

$$[\text{Fe}^{+2}] \cdot b_2 + [\text{Fe}^{+3}] \cdot b_3 = (C_{02} + C_{03}) \cdot \frac{V_0}{V_0 + V} \quad (140)$$

Then we get

$$E = E_0^* - a \cdot \ln \frac{b_3}{b_2} + a \cdot \ln \left(\frac{C_{03} \cdot V_{\text{eq}} + V}{C_{02}} \right) - a \cdot \ln(V_{\text{eq}} - V) \quad (141)$$

(compare with Eq. 115). Assuming $\theta = \ln \frac{b_3}{b_2} = \text{const}$, and applying Eq. 141 for two consecutive points (V_j, E_j) and (V_{j+1}, E_{j+1}) referred to this titration, we have

$$E_{j+1} - E_j = a \cdot \ln \left(\frac{C_{03} \cdot V_{\text{eq}} + V_{j+1}}{C_{02}} \right) - a \cdot \ln \left(\frac{V_{\text{eq}} - V_{j+1}}{V_{\text{eq}} - V_j} \right) \quad (142)$$

Denoting

$$x_{1j} = \frac{V_{j+1} - V_j}{C_{03} \cdot V_{\text{eq}} + V_j}; \quad x_{2j} = \frac{V_{j+1} - V_j}{V_{\text{eq}} - V_j} \quad (143)$$

from Eq. 142 we get

$$E_{j+1} - E_j = a \cdot \ln(1 + x_{1j}) - a \cdot \ln(1 - x_{2j}) \quad (144)$$

Applying the approximation 122, after transformations we get, by turns,

$$E_{j+1} - E_j = a \cdot \frac{1}{\frac{1}{2} + \frac{C_{03} \cdot V_{\text{eq}} + V_j}{C_{02}}} - a \cdot \frac{1}{\frac{1}{2} - \frac{V_{\text{eq}} - V_j}{V_{j+1} - V_j}}$$

$$\frac{E_{j+1} - E_j}{V_{j+1} - V_j} = a \cdot \left(\frac{1}{V_j^* + \frac{C_{03} \cdot V_{\text{eq}}}{C_{02}}} + \frac{1}{V_{\text{eq}} - V_j^*} \right)$$

$$\frac{E_{j+1} - E_j}{V_{j+1} - V_j} = a \cdot \left(\frac{V_{\text{eq}}(C_{02} + C_{03})}{(C_{02} \cdot V_j^* + C_{03} \cdot V_{\text{eq}})(V_{\text{eq}} - V_j^*)} \right)$$

$$u_j = \frac{V_{j+1} - V_j}{E_{j+1} - E_j} = \frac{C_{03} \cdot V_{\text{eq}} + C_{02} \cdot V_j^*}{a \cdot V_{\text{eq}} \cdot (C_{02} + C_{03})} \cdot (V_{\text{eq}} - V_j^*)$$

$$u_j = P + Q \cdot V_j^* - R \cdot V_j^{*2} + \varepsilon_j \quad (145)$$

where $\Phi_{\text{eq}} = \frac{1}{5}$,

$$P = \frac{C_{02} \cdot C_{03} \cdot V_0}{5 \cdot a \cdot C \cdot (C_{02} + C_{03})}; Q = \frac{C_{02} - C_{03}}{a \cdot (C_{02} + C_{03})}; R = \frac{5 \cdot C}{a \cdot (C_{02} + C_{03}) \cdot V_0} \quad (146)$$

and ε_j is the difference between the u_j value found from measurements and the $u(V_j^*)$ value found at $V = V_j^*$ from the model (145) assumed. Then we calculate

$$\frac{P}{R} = \left(\frac{V_0}{5C} \right)^2 \cdot C_{02} \cdot C_{03}; \quad \frac{Q}{R} = \frac{V_0}{5C} \cdot (C_{02} - C_{03}) \quad (147)$$

$$(A) C_{02} = \frac{5 \cdot C}{2 \cdot V_0} \cdot \left[\sqrt{\left(\frac{Q}{R} \right)^2 + 4 \cdot \frac{P}{R}} + \frac{Q}{R} \right];$$

$$(B) C_{03} = \frac{5 \cdot C}{2 \cdot V_0} \cdot \left[\sqrt{\left(\frac{Q}{R} \right)^2 + 4 \cdot \frac{P}{R}} - \frac{Q}{R} \right] \quad (148)$$

One should note that the factor $a = \frac{g}{\ln 10}$ in Eq. 141 and in the formulas for P, Q, R (Equations 146) does not enter the

expression for $\frac{P}{R}$ and $\frac{Q}{R}$ (Equations 147), i.e., the values for C_{02} and C_{03} (Equations 148) are not biased by the a -value that may differ, to some extent, from the Nernstian value, $a_0 = \frac{RT}{F}$, for electrodes commonly applied in potentiometric titrations [57].

Compact formulas needed for calculation of the C_{02} and C_{03} values on the basis of Eq. 148 are obtained if equal, consecutive portions $V_{j+1} - V_j = \Delta V$ of the titrant are added, i.e., $V_j = j \cdot \Delta V$,

$j=1, \dots, N$, $V_j^* = \frac{2j+1}{2} \cdot \Delta V$, and:

$$\sum_{j=1}^{N-1} V_j^{*k} = \left(\frac{\Delta V}{2} \right)^k \cdot \sum_{j=1}^{N-1} (2j+1)^k = \left(\frac{\Delta V}{2} \right)^k \cdot \left[\sum_{j=1}^N (2j+1)^k - 1 \right]$$

The following formulas [16] are applicable here:

$$\sum_{j=1}^N (2j-1) = N^2; \sum_{j=1}^N (2j-1)^2 = \frac{1}{3} \cdot N(4N^2 - 1)$$

$$\sum_{j=1}^N (2j-1)^3 = N^2(2N^2 - 1); \sum_{j=1}^N (2j-1)^4 = \frac{1}{15} \cdot N(4N^2 - 1)(12N^2 - 7)$$

Then we have:

$$\frac{P}{R} = \left(\frac{\Delta V}{2} \right)^2 \cdot \frac{\begin{matrix} \sum_{j=1}^{N-1} u_j & \sum_{j=1}^{N-1} (2j+1) & \sum_{j=1}^{N-1} (2j+1)^2 \\ \sum_{j=1}^{N-1} (2j+1) \cdot u_j & \sum_{j=1}^{N-1} (2j+1)^2 & \sum_{j=1}^{N-1} (2j+1)^3 \\ \sum_{j=1}^{N-1} (2j+1)^2 \cdot u_j & \sum_{j=1}^{N-1} (2j+1)^3 & \sum_{j=1}^{N-1} (2j+1)^4 \end{matrix}}{\begin{matrix} \sum_{j=1}^{N-1} u_j & \sum_{j=1}^{N-1} (2j+1) & N-1 \\ \sum_{j=1}^{N-1} (2j+1) \cdot u_j & \sum_{j=1}^{N-1} (2j+1)^2 & \sum_{j=1}^{N-1} (2j+1) \\ \sum_{j=1}^{N-1} (2j+1)^2 \cdot u_j & \sum_{j=1}^{N-1} (2j+1)^3 & \sum_{j=1}^{N-1} (2j+1)^2 \end{matrix}}$$

$$\frac{Q}{R} = \frac{\Delta V}{2} \cdot \frac{\begin{matrix} \sum_{j=1}^{N-1} u_j & N-1 & \sum_{j=1}^{N-1} (2j+1)^2 \\ \sum_{j=1}^{N-1} (2j+1) \cdot u_j & \sum_{j=1}^{N-1} (2j+1) & \sum_{j=1}^{N-1} (2j+1)^3 \\ \sum_{j=1}^{N-1} (2j+1)^2 \cdot u_j & \sum_{j=1}^{N-1} (2j+1)^2 & \sum_{j=1}^{N-1} (2j+1)^4 \end{matrix}}{\begin{matrix} \sum_{j=1}^{N-1} u_j & \sum_{j=1}^{N-1} (2j+1) & N-1 \\ \sum_{j=1}^{N-1} (2j+1) \cdot u_j & \sum_{j=1}^{N-1} (2j+1)^2 & \sum_{j=1}^{N-1} (2j+1) \\ \sum_{j=1}^{N-1} (2j+1)^2 \cdot u_j & \sum_{j=1}^{N-1} (2j+1)^3 & \sum_{j=1}^{N-1} (2j+1)^2 \end{matrix}}$$

For further details, see ref. [16].

All the modifications of the Gran methods were suggested/introduced by Michałowski [16-19], and extended on different acid-base systems, involved also with total alkalinity [44,58,59], and carbonate alkalinity [60], in particular.

Final Comments

Redox systems are the most important and most complex electrolytic systems. The transfer of electrons is usually accompanied by other (acid-base, complexation and precipitation) reactions. The complexity of redox systems is expressed by the number of equilibrium constants, and by diversity of these constants involved with the system

considered. In all instances, it is important to provide a consistent approach, where the systems of different complexity are elaborated in a uniform manner according to GATES principles [1], formulated by Michałowski (1992) [35–38].

When related to redox systems, the acronym GATES/GEB \in GATES is applied. The GATES/GEB is perceived as the best possible thermodynamic approach to redox systems, and the GEB is the Law of Nature. The GEB, discovered by Michałowski, and formulated as the Approaches I (1992) and II (2005) to GEB, is fully compatible with charge and concentration balances, and relations for the corresponding equilibrium constants. GEB completes the set of K equations needed for mathematical description of redox systems, on the basis of calculations made according to an iterative computer program.

Both Approaches to Generalized Electron Balance (GEB) are equivalent, i.e.,

Approach I to GEB \Leftrightarrow Approach II to GEB

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

The Approach I to GEB is based on the principle of common pool of electrons involved with electron-active elements [1,3,5], whereas the Approach II to GEB originates from the linear combination $f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(O) - f(H)$ of elemental balances: $f_1 = f(H)$ for H, and $f_2 = f(O)$ for O, formulated for a redox system. For non-redox systems, $2 \cdot f(O) - f(H)$ is a linear combination of other balances: charge balance $f_0 = \text{ChB}$, and elemental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$), where element/core $Y_k \neq H, O$. For a redox system, $f_0, f_{12}, f_3, \dots, f_K$ is a set of K linearly independent equations, whereas for a non-redox system we have the set of $K - 1$ linearly independent equations f_0, f_3, \dots, f_K .

When compared with the Approach I, the Approach II to GEB offers several advantages. Although derivation of GEB according to the Approach II is more laborious (time-consuming), it enables to formulate this balance without prior knowledge of oxidation numbers (ON's) for the elements, involved frequently in complex components and species of the system. The composition (expressed by chemical formula) of components forming the system and of the species formed in the system, together with their external charges, are required; it provides an information sufficient to formulate the GEB. It is the paramount advantage of the Approach II to GEB over the Approach I to GEB, where prior knowledge of ON's is needed [16–19,27,35–38]. Anyway, the ON, representing the degree of oxidation of an element in a compound or in a species is a contractual concept. In this regard, formulation of GEB according to Approach II is far more useful than the Approach I when applied to complex organic species in redox systems of biological origin [61–65].

The Approach II to GEB is advantageous/desired, *inter alia*, for redox systems where radical and ion-radical species are formed. What is more, the players and fans, as ones perceived from the Approach I to GEB viewpoint, are not indicated *a priori* within the Approach II to GEB. The Approach I, considered as a “short” version of GEB, is more convenient when oxidation

numbers for all elements of the system are known beforehand. Within the Approaches I and II to GEB, the roles of oxidants and reductants are not ascribed *a priori* to particular components forming the redox system, and to the species formed in this system. In other words, full ‘democracy’ is established *a priori* within GATES/GEB, where oxidation number, oxidant, reductant, equivalent mass, and stoichiometric reaction notation are the redundant concepts only. The fact that $f_{12} = 2 \cdot f(O) - f(H)$ is the primary form of GEB indicates clearly the exquisite role of H and O in redox systems, especially in aspect of insignificantly small concentrations of free electrons, as those calculated and discussed in [11] (pp. 361–363).

To check the linear dependency of equations related to a non-redox system, the transformation of the linear combination into identity, $0 = 0$, is suggested. For this purpose, we formulate the linear combination (Eq. 7)

$$\sum_{k=1}^K d_k \cdot f_k - f_0 = 0 \quad (149)$$

where $d_1 = +1$, $d_2 = -2$, ... In general, d_k is equal to (or involved with) the oxidation numbers of the k -th element in the corresponding component and species [33,34]. The multipliers d_k ($k=1,2,3,\dots,K$) enable to get the desired form of the linear combination: for a non-redox system, the desired linear combination is the identity $0 = 0$; it particularly refers to subsystems D and T, considered in sections: I-1, I-2; II-1, II-2; III-1, III-2. For a redox system it is the simpler form of the linear combination, e.g., Eq. 22a. Further combinations with balances for electron-active elements may give simpler forms of GEB, e.g., Eq. 25a or Eq. 27.

In some other instances, D and/or T are redox subsystems; e.g. Br_2 disproportionates in D considered in [31,33,35,36]. Iodine (as HIO , NaIO) disproportionates in D considered in [21,22,25], and iodine (as $\text{I}_2 + \text{KI}$) disproportionates in T considered in [20,23]. Disproportionating and symproportionating systems are considered in [15].

When the D and T, considered in sections: I-1, I-2; II-1, II-2; III-1, III-2 are mixed, the redox reactions occur in the D+T mixture. In this paper, the D+T mixture is formed gradually, according to titrimetric mode, where T is added dropwise into D.

In the redox D+T system, considered as the system I-3 (section 2), we have Fe and Ce as players, and H, O, S, C as fans. Generally, in the set of K elements of the system we have K^* fans, and $K - K^*$ players. Applying the summation

$$\sum_{k=1}^{K^*} d_k \cdot f_k - f_0 = 0 \quad (150)$$

we get the simpler form of the linear combination, where the multipliers for the numbers/concentrations of the species and components containing the players are equal to ON's for elements in these species and components, see Equations 22 and 22a; the components and species composed only from fans are not involved in Equations 22 and then in 22a. This regularity is valid for any redox system. For a non-redox system ($K^* = K$), Eq. 150 is transformed into identity, $0 = 0$. For any redox system, Eq. 150 is different from the identity. The identity 0

$= 0$ is the useful criterion of linear dependence of balances. The set of K balances $f_0, f_{1,2}, f_3, \dots, f_K$ is mutually independent for redox systems, or mutually dependent for non-redox systems. This is the general criterion distinguishing between redox and non-redox system. For a non-redox system, $K - 1$ independent balances f_0, f_3, \dots, f_K are formulated. These regularities are obligatory for static and dynamic systems. In all instances, the balances are ultimately expressed in terms of molar concentrations of compounds and species. This results from the fact that the equilibrium constants are expressed in terms of molar concentrations of the species, see e.g. the relations 28.

The GATES provides the powerful tool necessary for thermodynamic description of equilibrium, non-equilibrium, and metastable, redox and non-redox, mono- and two-phase systems of any degree of complexity, with the possibility of all attainable/pre-selected physicochemical knowledge to be involved, with none simplifying assumptions done for calculation purposes, where different types of reactions occur in batch/static or dynamic systems. In all instances, one can check/follow measurable quantities (E , pH) in dynamic and static systems, and gain an information about details not measurable in real experiments (Figure 19b); it particularly refers to dynamic speciation diagrams. Different “variations on the theme” are also possible; it particularly refers to metastable redox systems [1,11]. GATES/GEB is also the first step for resolution of kinetic systems, e.g. ones where oscillation reactions occur [1,38].

Formulation of GATES and GATES/GEB in particular, has allowed to sort out many important concepts, based previously on the stoichiometry of a reaction. And so, the Generalized Equivalent Mass (GEM) concept, also introduced by Michałowski (1979), has been suggested [4,8,44], with none relevance to a chemical reaction notation. The formulation of dynamic buffer capacities for redox systems [31] is fully compatible with the dynamic buffer capacity related to the systems, where only acid-base equilibria are involved [33,44,66].

A general property of electrolytic systems (aqueous solutions) is indicated. Namely, it is stated that linear combination of elemental balances for hydrogen (H) and oxygen (O) gives an equation that is linearly independent on other (charge and concentration) balances when referred to redox systems. This new balance is equivalent to the electron balance (Generalized Electron Balance, GEB), discovered by Michałowski. The GEB is considered as a law of matter conservation, referred to electrolytic systems. Analogous combination for H and O, when referred to non-redox systems, gives an equation that is linearly dependent on charge and concentration balances. Both cases are exemplified below.

The complex dynamic redox systems are considered in this paper. For example, system III-3 includes 41 species and 31 equilibrium constants, while system V has 47 species involves in 34 equilibrium constants. Formation of precipitates was also taken into account in these systems. All attainable (qualitative and quantitative) physicochemical knowledge was involved in the related balances and expressions for the corresponding equilibrium constants. The degree of complexity of these

systems was comparable or exceeded the complexity of the system in which $KIO_3 + HCl + H_2SeO_3 + HgCl_2$ solution was titrated with ascorbic acid ($C_6H_8O_6$) solution, see e.g. [1,42]. Moreover, the computer programs formulated within GATES/GEB are open ones after taking into account the addition of new (or correction of old) physicochemical knowledge about the systems. Furthermore, the programs offer different variations related to changes in the concentrations of components or volumes. Different “variations on the theme” can also be carried out, which are associated to the opening/closing of the reaction paths in metastable systems. The speciation diagrams make it possible to formulate the reactions taking place at any stage of titration, as well as their relative efficiencies.

System V is an example where the species present in the sample titrated (titrand, D) and those formed during the titration interact leading to the formation of soluble or insoluble (precipitates) complexes. In the system III-3, Fe^{+2} ions form oxalate complexes in D, while in the D+T system new oxalate complexes formed by Mn^{+3} ions are also included in considerations. All known sulphate complexes are also incorporated into the related balances, next to the hydroxo- and proto-complexes.

In the Systems I – III, the carbonate species were purposely introduced into consideration (as admixtures) to indicate the necessity to formulate a common balance for oxalate and carbonate species (Eq. 52); the carbonate species formed by oxidation of oxalate species in the system III-3 are indistinguishable from the ones originating from the admixture, and must be formulated in the common balance (Eq. 52). In contrast, in the case of the subsystem III-2, carbonates and oxalates can be formulated in separate balances.

The System IV provides an example of optimizing *a priori*, and therefore it is based on full preliminary physicochemical knowledge, not on the knowledge obtained *a posteriori*, on experimental way. It also allows to suggest new terms of the analysis. In the present case, it concerns the effect of H_2SO_4 concentration (C_{oi}) on the result of the analysis. By the way, it is possible – in this case – to suggest an optional solution, involved with recording another end point of titration, at a different stoichiometry of the reaction between analyte and reagent.

The simulated titration offers also huge advantages, of cognitive and didactic nature. On the basis of the relevant $E = E(\Phi)$ curves, one can select the appropriate $\Phi = \Phi_{eqi}$ values, where abrupt changes in the potential E value occur. Moreover, on the basis of changes (decrease, growth) of concentrations of the major components on the speciation diagrams, an appropriate stoichiometric reaction can be formulated, and the relative effectivity of associated/concurrent reactions can be evaluated. This approach is represented by the Generalized Equivalence Mass (GEM) concept [1,4,8,10,11] providing a reasonable alternative to the equivalence weight concept suggested by the IUPAC, based on the stoichiometric reaction notation which plays, generally, the role of a “dummy”.

The System V is interesting mainly because of the formation

of sparingly soluble precipitate **CuI**, as a factor in this system that causes the change in the general direction of the redox reaction. Specifically, a cursory assessment of the standard potential values (E_{oi} , V) for half-reactions (0.153 for $\text{Cu}^{+2} + e^{-1} = \text{Cu}^{+1}$, 0.621 for $\text{I}_2 + 2e^{-1} = 2\text{I}^{-1}$, 0.545 for $\text{I}_3^{-1} + 2e^{-1} = 3\text{I}^{-1}$ and 0.536 for $\text{I}_{2(\text{s})} + 2e^{-1} = 2\text{I}^{-1}$) leads to the conclusion that iodine (I_2 , I_3^{-1} or $\text{I}_{2(\text{s})}$), as a form of higher standard potential value, should oxidize Cu^{+1} to Cu^{+2} , which would then be expressed by the virtual reaction, e.g., $\text{I}_3^{-1} + 2\text{Cu}^{+1} = 3\text{I}^{-1} + 2\text{Cu}^{+2}$. To recap: such a case could take place under the (virtual) assumption that the **CuI** precipitate (with its solubility product value) is not formed in the system in question. The real behaviour of the system is also (partly) ascribed to the stability constant of the species CuI_2^{-1} ; the sparingly soluble **CuI** and the soluble complex CuI_2^{-1} are the causative agents affecting the direction of the redox reaction.

System V, on the stage 4^o, has sulphur species with different cores: SO_4^{-2} , $\text{S}_2\text{O}_3^{-2}$ and $\text{S}_4\text{O}_6^{-2}$. The sulphate species (i.e., with the core SO_4^{-2}) are not transformed into other sulphate species in a (virtual) synproportionation with thiosulphate or tetrathionate, or in reactions with other species in the system in question. Such a transformation occurs between thiosulphate and tetrathionate species (Equations 78, 79), and then they are involved in the common balance (Eq. 91a).

Iodometric reactions are rapid and quantitative. The reaction between iodine and the thiosulphate ions $\text{I}_2 + 2\text{S}_2\text{O}_3^{-2} = 2\text{I}^{-1} + \text{S}_4\text{O}_6^{-2}$ proceeds quantitatively in neutral or mildly acidic solutions, where the thiosulphate species are in a metastable state. In strongly acidic solutions, the thiosulphuric acid disproportionates according to the scheme $\text{H}_2\text{S}_2\text{O}_3 = \text{H}_2\text{SO}_3 + \text{S}$ [67]. This leads to errors because the stoichiometry of the reactions differs from that shown above, which then makes the control of pH important. For this purpose, the acidified solution of copper salt was neutralized with ammonia (stage 1^o), and then adjusted to a weakly acidic reaction with acetic acid (stage 2^o). The thiosulphate ions can also be metabolized/destroyed by some micro-organisms (e.g., **S** transferase). In such cases, the problems involved with metastable electrolytic redox systems are relevant again.

Testing complex redox (and non-redox) systems using iterative computer programs merits wider attention from chemists, so that some analytical procedures may be optimised and the best *a priori* conditions for analyses may be chosen. Results obtained from equilibrium (thermodynamic) simulated analysis can always be considered as a reference for the real behaviour of the system tested, which is frequently corrupted by kinetic phenomena.

The GATES/GEB is completely opposite to the approaches used previously, where two pairs of redox species were selected as “responsible” for the reaction occurring in a system; these were usually minor components. Within GATES and GATES/GEB in particular, the reactions occurred in a system can be formulated on the basis of speciation diagrams (particularly: dynamic speciation diagrams) obtained from calculations performed according to principles assumed in GATES.

The GATES/GEB provides a powerful tool for increasing thermodynamic knowledge about electrolytic redox systems, and is incomparably better than that offered hitherto by the well-known Pourbaix diagrams [68]. Such knowledge stems from the results of calculations obtained by the implementation of iterative computer programs, e.g., the ones offered by MATLAB software for GATES and GATES/GEB purposes.

Contrary to appearances, established by the current paradigm “obligatory” till now, the criterion distinguishing non-redox and redox systems is not immediately associated with free electrons in the system. The new/fundamental/practical criterion involved with $f_{12} = 2 \cdot f(\text{O}) - f(\text{H})$ and its properties, unknown in earlier literature, provides a kind of uniformity in the formulas derived for this purpose. This fact, especially the simple calculations of free electron concentrations in redox systems [11], deny the unique role of free electrons in redox reactions, expressed in elementary redox reactions, as described in half- or partial reactions, where the species of the same element with different oxidation numbers are involved. On the other hand, it points to the unique role of H and O in redox systems [2], suggested elsewhere, in earlier theoretical/hypothetical considerations on these systems. Here is the hidden simplicity, which had to be discovered, as the Approach II to GEB. The author TM contends that the discovery of the Approach II GEB would most likely be impossible without the prior discovery of the Approach I to GEB. The GEB concept, valid for electrolytic redox systems, is the emanation of balances for H and O, referred to aqueous media. GEB is compatible with other (charge and concentration) balances and enables to resolve the electrolytic (mono- or/and two-phase) redox systems of any degree of complexity, within the scope of GATES, perceived as the thermodynamic approach to equilibrium and metastable systems, where all necessary physicochemical knowledge on the systems tested is involved. The GATES is perceived as the unrivalled tool applicable, among others: (a) to mathematical modelling of thermodynamic behavior of the systems, (b) in choice of optimal *a priori* conditions of chemical analyses, and (c) in gaining chemical information invisible in real experiments, in general.

GATES/GEB is a counter-proposal in relation to earlier IUPAC decisions, presented in three subsequent editions of the *Orange Book*, and based on the reaction stoichiometry; that viewpoint was criticized unequivocally/exhaustively/convincingly, especially in a series of review articles [1,3-6,9-11]. It were demonstrated, on examples of redox systems of different complexity, that stoichiometry is a secondary/derivative/“fragile” concept, from the viewpoint of GATES, and GATES/ GEB, in particular.

Conservation laws of physics are very closely related to the symmetry of physical laws under various transformations. The nature of these connections is an intriguing physical problem. The theory of these connections, as it appears in classical physics, constitutes one of the most beautiful aspects of mathematical physics. It confirms a general theorem of Emmy Noether which states that symmetries and conservation laws of a physical system correspond to each other [69]. The

Noether's conceptual approach to algebra led to a body of principles unifying algebra, geometry, linear algebra, topology, and logic. The theory of this connection constitutes one of the most beautiful chapters of mathematical physics.

Concluding, GATES is the overall, thermodynamic approach to redox and non-redox, static and dynamic, single and multiphase equilibrium, metastable and non-equilibrium electrolytic systems, of any degree of complexity. Possibilities of GATES/GEB are far greater than ones offered by the actual physicochemical knowledge related to the system in question. Summarizing, in terms of its content, this paper offers the best possible ways to resolution of the issues raised.

Instead of Epilogue

The function of Science is to discover general regularities in Nature, and to find the rules governing them. Although ignorance more frequently instigates confidence than does knowledge, being ignorant is not a shame in the degree, as the reluctance to learn it is; a man is responsible for his ignorance.

Like history, the science is factually a set of lies agreed upon. There are two ways to be fooled: one is to believe what is not true, the other is to refuse to believe what is true. Humans see what they want to see. The most difficult thing to explain are the vividly evident things that everyone has decided not to see.

However, it is better to know the truth than to delude ourselves with beautiful lies. Real knowledge is to know the extent of one's ignorance (Confucius). We are all born ignorant, but one must work hard to not remain stupid (B. Franklin). Truth is the only thing that people don't believe.

The great characters' passion is the great ambition. To become a real chemist, you want to take the Science and math; those are the main things. The Science is stateless, because it belongs to all humanity; it is like the torch which illuminates the World (L. Pasteur).

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