The modified Gran methods in potentiometric redox titrations derived according to GATES/GEB principles

ABSTRACT: The paper concerns the modified Gran methods, designed for determination of equivalence volume ($V_{eq}$) and the slope ($J$) value of a redox indicator electrode (RIE) applied for potentiometric titrations in redox systems. The methods are exemplified by the titration of (1°) $\text{FeSO}_4$ and (2°) $\text{FeSO}_4 + \text{Fe}_2(\text{SO}_4)_3$ mixture with $\text{KMnO}_4$ or $\text{Ce}(\text{SO}_4)_2$ solution as titrant. The modified Gran methods are based on detailed conclusions resulting from thermodynamic modelling of the related systems according to GATES/GEB principles.

KEYWORDS: Redox titration; GATES/GEB; modified Gran methods; electrode calibration.

INTRODUCTION
The original versions of the Gran I [1,2] and Gran II [3,4] methods, denoted later as G(I) and G(II) methods (for brevity), were designed for evaluation of equivalence volume ($V_{eq}$) in potentiometric titrations, based on transformation of fragments of S-shaped titration curve into linear segments. Both methods, of extrapolative nature (extrapolative standard addition method), especially G(II) method, were widely exploited later in practice by chemists-analysts.
The progress in applications of the G(I) and G(II) methods for analytical purposes was not uniform when referred to the main areas of titrimetric analyses, i.e., acid-base, redox, complexation and precipitation titrations. The methods were devoted mainly 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. [5]. The functional dependencies based on those assumptions, gave erroneous experimental results for \( V_{eq} \), as were stated in [6-8], and confirmed later in the papers [9-12].

The modified Gran methods, based on the GATES/GEB [13-24] principles, will be illustrated on three examples of potentiometric redox titrations, T(V) \( \Rightarrow \) D(V_0). The redox systems considered in this paper will be denoted as follows:

**System I:** \( \text{KMnO}_4 \text{(C)} + \text{CO}_2 \text{(C}_2\text{)} \Rightarrow \text{FeSO}_4 \text{(C}_02\text{)} + \text{H}_2\text{SO}_4 \text{(C}_04\text{)} + \text{CO}_2 \text{(C}_05\text{)} \),

**System II:** \( \text{KMnO}_4 \text{(C)} + \text{CO}_2 \text{(C}_2\text{)} \Rightarrow \text{FeSO}_4 \text{(C}_02\text{)} + \text{Fe}_2\text{(SO}_4\text{)}_3 \text{(C}_03\text{)} + \text{H}_2\text{SO}_4 \text{(C}_04\text{)} + \text{CO}_2 \text{(C}_05\text{)} \),

**System III:** \( \text{Ce(SO}_4\text{)}_2 \text{(C)} + \text{H}_2\text{SO}_4 \text{(C}_1\text{)} + \text{CO}_2 \text{(C}_2\text{)} \Rightarrow \text{FeSO}_4 \text{(C}_02\text{)} + \text{H}_2\text{SO}_4 \text{(C}_04\text{)} + \text{CO}_2 \text{(C}_05\text{)} \),

where \( C, C_02, C_03, C_04, C_05 \) are concentrations [mol/L] of the corresponding solutes in T and D, respectively, completed by water. From formal viewpoint, the System I can be considered as a particular case of the System II, at \( C_03 = 0 \). Some similarities inherent in the balances will be applied for further presentation of the balances in a compact form.

The detailed considerations regarding the modified Gran methods will be preceded by formulation of the Generalized Electron Balance (GEB) for the Systems II and III, according to the Approach II to GEB. The algebraic equivalency of Approaches I and II to GEB will also be proved.

### 2. Components and species

The terms: components of the system and species in the system are distinguished. After mixing the components (solvent + solutes), a mixture of defined species \( X_i^Z \) is formed.

We refer here to aqueous electrolytic systems, where the species \( X_i^Z \) exist as hydrates \( X_i^{Z \cdot n_{iW}} \), \( i=1,\ldots, I; z_i = 0, \pm 1, \pm 2, \ldots \) is a charge, expressed in elementary charge units, \( e = F/N_A \) (F = 96485 C mol\(^{-1}\) – Faraday’s constant, \( N_A = 6.022 \times 10^{23} \) mol\(^{-1}\) – Avogadro’s number), \( n_i = n_{iW} = n_i\text{H}_2\text{O} \geq 0 \) is a mean number of water (W=\text{H}_2\text{O}) molecules attached to \( X_i^Z \); the case \( n_{iW} = 0 \) is then also admitted.

For some reasons, it is justifiable to start the balancing from the numbers of particular entities: \( N_{0j} \) – for components (\( j = 1,\ldots, J \)) represented by molecules, and \( N_i \) – for the species \( X_i^{Z \cdot n_{iW}} \) (ions and molecules) of \( i \)-th kind (\( i = 1,\ldots, I \)). The mono- or two-phase electrolytic system thus obtained involves \( N_1 \) molecules of \( \text{H}_2\text{O} \) and \( N_i \) species of \( i \)-th kind, \( X_i^{Z \cdot n_{iW}} \) (\( i=2, 3, \ldots, I \)), specified briefly as \( X_i^Z (N_i, n_i) \), where \( n_i = n_{iW} = n_i\text{H}_2\text{O} \). For ordering purposes, we write: \( H^+ (N_2, n_2), \text{OH}^- (N_3, n_3), \ldots \), where \( z_2 = 1, z_3 = -1, \ldots \).

The System II involves the non-redox subsystems:

- (II.1) \( T(V) \) subsystem, composed of \( \text{KMnO}_4 \text{(N}_01\text{)} + \text{H}_2\text{O} \text{(N}_02\text{)} + \text{CO}_2 \text{(N}_03\text{)} \);
- (II.2) \( D(V_0) \) subsystem, composed of \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \text{(N}_04\text{)} + \text{Fe}_2\text{(SO}_4\text{)}_3 \cdot x\text{H}_2\text{O} \text{(N}_05\text{)} + \text{H}_2\text{SO}_4 \text{(N}_06\text{)} + \text{H}_2\text{O} \text{(N}_07\text{)} + \text{CO}_2 \text{(N}_08\text{)} \).

For I.2, we have \( N_{05} = 0 \) in the \( D(V_0) \) subsystem.

The System III involves the non-redox subsystems:

- (III.1) \( T(V) \) subsystem, composed of \( \text{Ce(SO}_4\text{)}_2 \cdot 4\text{H}_2\text{O} \text{(N}_01\text{)} + \text{H}_2\text{SO}_4 \text{(N}_02\text{)} + \text{H}_2\text{O} \text{(N}_03\text{)} + \text{CO}_2 \text{(N}_04\text{)} \);
- (III.2) \( D(V_0) \) subsystem, composed of \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \text{(N}_05\text{)} + \text{H}_2\text{SO}_4 \text{(N}_06\text{)} + \text{H}_2\text{O} \text{(N}_07\text{)} + \text{CO}_2 \text{(N}_08\text{)} \).
The common list of species, that will be applied/selected to particular Systems (I, II, III), is as follows:

\[ \begin{align*}
&\text{H}_2\text{O} (\text{N}_1); \text{H}^+ (\text{N}_2, \text{n}_2); \text{OH}^- (\text{N}_3, \text{n}_3); \text{HSO}_4^- (\text{N}_4, \text{n}_4); \text{SO}_4^{2-} (\text{N}_5, \text{n}_5); \text{H}_2\text{CO}_3 (\text{N}_6, \text{n}_6); \text{HCO}_3^- (\text{N}_7, \text{n}_7); \\
&\text{CO}_3^{2-} (\text{N}_8, \text{n}_8); \text{Fe}^{2+} (\text{N}_9, \text{n}_9), \text{FeOH}^{+1} (\text{N}_{10}, \text{n}_{10}); \text{FeSO}_4 (\text{N}_{11}, \text{n}_{11}); \text{Fe}^{3+} (\text{N}_{12}, \text{n}_{12}); \text{FeOH}^{2+} (\text{N}_{13}, \text{n}_{13}); \\
&\text{Fe(OH)}^{2+} (\text{N}_{14}, \text{n}_{14}); \text{Fe}_2(\text{OH})_2^{+4} (\text{N}_{15}, \text{n}_{15}); \text{FeSO}_4^{1+} (\text{N}_{16}, \text{n}_{16}); \text{Fe(SO}_4)_2^{2-} (\text{N}_{17}, \text{n}_{17}) ; \\
&\text{K}^{+1} (\text{N}_{18}, \text{n}_{18}); \text{MnO}_4^{-1} (\text{N}_{19}, \text{n}_{19}); \text{MnO}_3^{2-} (\text{N}_{20}, \text{n}_{20}); \text{Mn}^{3+} (\text{N}_{21}, \text{n}_{21}); \text{MnOH}^{+2} (\text{N}_{22}, \text{n}_{22}); \text{Mn}^{2+} (\text{N}_{23}, \text{n}_{23}) ; \\
&\text{MnOH}^{+1} (\text{N}_{24}, \text{n}_{24}); \text{MnSO}_4 (\text{N}_{25}, \text{n}_{25}); \text{Ce}^{4+} (\text{N}_{26}, \text{n}_{26}); \text{CeOH}^{+3} (\text{N}_{27}, \text{n}_{27}); \text{Ce}_2(\text{OH})_3^{+5} (\text{N}_{28}, \text{n}_{28}) ; \\
&\text{Ce}_2(\text{OH})_4^{+4} (\text{N}_{29}, \text{n}_{29}); \text{CeSO}_4^{2+} (\text{N}_{30}, \text{n}_{30}); \text{Ce}^{5+} (\text{N}_{31}, \text{n}_{31}); \text{Ce}^{3+} (\text{N}_{32}, \text{n}_{32}); \text{Ce}^{3+} (\text{N}_{33}, \text{n}_{33}); \\
&\text{CeOH}^{+2} (\text{N}_{34}, \text{n}_{34}); \text{CeSO}_4^{4+} (\text{N}_{35}, \text{n}_{35}); \text{Ce}^{3+} (\text{N}_{36}, \text{n}_{36}); \text{Ce}^{3+} (\text{N}_{37}, \text{n}_{37});
\end{align*} \]

The species, with the related ordinal numbers, will be applied in the balances, formulated below. Molar concentrations [mol/L] of the species \( x_i \) are denoted as \( [x_i] \), for brevity.

The presence of carbonate species is considered here as an effect of CO\(_2\) from air, as the admixture of ‘pure’ water used on the step of D and T preparation; it may imitate the real conditions of the analysis, realised according to titrimetric mode.

The T and D can be considered as static (sub)systems of the dynamic D+T system realised in the titration T(V) \( \square \) D(V\(_{\text{T}}\)), where V mL of T is added into V\(_0\) mL of D, up to a defined point of the titration, and V\(_0\)+V mL of D+T mixture is obtained at this point, if the additivity of the volumes is valid/tolerable. The D+T mixture is homogenized after each (small) consecutive portion of T added into D, to imitate the titration as the **quasistatic** process realised in a closed system, under isothermal conditions, pre-assumed for modelling purposes.

### 3. Notation of balances

In aqueous media, we formulate charge balance, \( f_0 = \text{ChB} \), and elemental balances: \( f_i = f(\text{H}) \) for \( E_i = \text{H} \) (hydrogen) and \( f_i = f(\text{O}) \) for \( E_i = \text{O} \) (oxygen),... ; other elemental or core balances are denoted as \( f_k = f(Y_k) \), \( Y_k = E_k \) or \( \text{core}_k \) (k=3,...,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; e.g., \( \text{SO}_4^{2-} \) is a core within the set of sulfate species: \( \text{HSO}_4^- \cdot \text{n}_4 \text{H}_2\text{O} \), \( \text{SO}_4^{2-} \cdot \text{n}_4 \text{H}_2\text{O} \), \( \text{FeSO}_4 \cdot \text{n}_4 \text{H}_2\text{O} \) in the (I.2) D(V\(_0\)) subsystem.

In order to formulate the reliable (formally correct) set of 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, when regarding the preparation of the appropriate solutions; e.g., \( \text{Ce}^{3+} \cdot 4\text{H}_2\text{O} \) is dissolved in \( \text{H}_2\text{SO}_4 \) solution, not in water.

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

\[
\begin{align*}
&f_k = \sum_{i=1}^{\text{K}} a_{ki} \cdot N_i - \sum_{j=1}^{\text{K}} b_{kj} \cdot N_{oj} = 0 \quad \Rightarrow \quad \sum_{i=1}^{\text{K}} a_{ki} \cdot N_i = \sum_{j=1}^{\text{K}} b_{kj} \cdot N_{oj} \\
&f_k = \sum_{i=1}^{\text{K}} a_{ki} \cdot N_i - \sum_{j=1}^{\text{K}} b_{kj} \cdot N_{oj} = 0 \quad \Rightarrow \quad \sum_{j=1}^{\text{K}} b_{kj} \cdot N_{oj} = \sum_{i=1}^{\text{K}} a_{ki} \cdot N_i
\end{align*}
\]

for elements with negative oxidation numbers, or

for elements with positive oxidation numbers, \( k \in 3,...,K \). 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.

### 4. Formulation of balances for the System II

The balances are as follows:

\( f_0 = \text{ChB} \)
Next, we can apply the combination of equations 4, 6 and 10, giving the shortest form of GEB
\[
Z_{Z} = 7N_{2}^{2}(N_{2}^{2}f - N_{2} + N_{2}f) + 2N_{12}n_{11} + 2N_{12}n_{12} + N_{13}(1+2n_{13}) + N_{14}(2+2n_{14}) + N_{15}(2+2n_{15}) + 2N_{16}n_{16} + 2N_{17}n_{17} + 2N_{18}n_{18} + 2N_{9}n_{9} + 2N_{10}n_{20} + 2N_{21}n_{21} + 2N_{22}(1+2n_{22}) + 2N_{23}n_{23} + 2N_{24}(1+2n_{24}) + 2N_{25}n_{25}
\]
= 2N_{02} + 14N_{04} + 2XN_{05} + 2N_{06} + 2N_{07}
\]
f_{2} = f(O)
\]
N_{1} + N_{2}n_{2} + N_{3}(1+n_{3}) + N_{4}(4+n_{4}) + N_{5}(8+(n_{5} + N_{6})(3+n_{6}) + N_{6}(3+n_{6}) + N_{8}(3+n_{6}) + N_{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}) + 2N_{21}n_{21} + 2N_{22}(1+n_{22}) + 2N_{23}n_{23} + 2N_{24}(1+n_{24}) + 2N_{25}(4+n_{25})
\]
= 4N_{01} + N_{02} + 2N_{03} + 11N_{04} + (12+x)N_{05} + 4N_{06} + 6N_{07} + 2N_{08}
\]
-f_{5} = f(SO_{4})
\]
N_{04} + 3N_{05} + N_{06} = N_{4} + N_{5} + N_{11} + N_{16} + 2N_{17} + N_{25}
\]
-f_{1} = f(CO_{3})
\]
N_{03} + N_{08} = N_{6} + N_{7} + N_{8}
\]
-f_{2} = f(Fe)
\]
N_{04} + 2N_{05} = N_{9} + N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + 2N_{15} + 2N_{16} + N_{17}
\]
-f_{6} = f(K)
\]
N_{01} = N_{18}
\]
-f_{3} = f(Mn)
\]
N_{01} = N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25}
\]
f_{12} = 2f_{2} - f_{1}
\]
-N_{2} + N_{3} + 7N_{4} + 8N_{5} + 4N_{6} + 5N_{7} + 6N_{8} + N_{10} + 8N_{11} + 13 + 2N_{14} + 2N_{15} + 8N_{16} + 16N_{17} + 8N_{19} + 8N_{20} + N_{22} + 8N_{25} = 8N_{01} + 4N_{03} + 8N_{04} + 24N_{05} + 6N_{06} + 4N_{08}
\]
2f_{2} - f_{1} + f_{6} - 6f_{5} - 4f_{4} - f_{8} = 0 \iff (1): f_{1} + f_{6} - 6f_{5} - 4f_{4} - f_{8} = 0 \iff (+1)f_{1} + (-2)f_{2} + (+6)f_{5} + (+4)f_{4} + (+1)f_{6} - f_{8} = 0 \iff (+1)f_{1}(-2)f_{2} + (+6)f_{5} + (+4)f_{4} + (+1)f_{6} - f_{8} = 0 \iff (-2)f_{2} + (+6)f_{5} + (+4)f_{4} + (+1)f_{6} - f_{8} = 0 \iff (-2)f_{2} + (+6)f_{5} + (+4)f_{4} + (+1)f_{6} - f_{8} = 0
\]
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_{04} + 6N_{05}
\]
Denoting the atomic numbers: Z_{Fe} = 26, Z_{Mn} = 25, from equations: 4, 6 and 9, we obtain the balance
\[
Z_{Fe}f_{3} + Z_{Mn}f_{1} - (2f_{2} - f_{1} + f_{6} - 6f_{5} - 4f_{4} - f_{8})
\]
(Z_{Fe} - 2)(N_{6} + 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_{04} + 2(Z_{Fe} - 3)N_{05} + (Z_{Mn} - 7)N_{01}
\]
Next, we can apply the combination of equations 4, 6 and 10, giving the shortest form of GEB
\[
3f_{5} + 2f_{2} - (f_{2} - f_{1} + f_{6} - 6f_{5} - 4f_{4} - f_{8}) = 0
\]
(N_{9} + N_{10} + N_{11}) - (5N_{19} + 4N_{20} + N_{21} + N_{22}) = N_{04} - 5N_{01}
\]
Applying the relations:
\[
[N_{0}^{X}] 
= 10^{3}N_{0}^{X} / N_{A}^{X}, \quad CV = 10^{3}N_{0}^{X} / N_{A}^{X}, \quad C_{2}V = 10^{3}N_{0}^{X} / N_{A}^{X}, \quad C_{0}V_{0} = 10^{3}N_{0}^{X} / N_{A}^{X}, \quad C_{0}V_{0} = 10^{3}N_{0}^{X} / N_{A}^{X}, \quad C_{0}V_{0} = 10^{3}N_{0}^{X} / N_{A}^{X}
\]
in the balances derived above, we have the optional/equivalent equations for GEB. From eq. 7, considered as the primary form of Generalized Electron Balance (GEB), f_{12} = pr-GEB, we obtain the equation
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\[
\begin{align*}
N_{35}(4+n_{13}) + N_{36}(8+n_{36}) + N_{37}(12+n_{37}) = 12N_{01} + 4N_{02} + N_{03} + 2N_{04} + 11N_{05} + 4N_{06} + N_{07} + 2N_{08} \\
-f_3 = -f(SO_4) \\
2N_{01} + N_{02} + N_{03} + N_{06} = N_4 + N_5 + N_{11} + N_{16} + 2N_{17} + N_{30} + 2N_{31} + 3N_{32} + N_{35} + 2N_{36} + 3N_{37} \\
-f_4 = -f(\text{CO}_3) \\
N_{04} + N_{08} = N_6 + N_7 + N_8 \\
-f_5 = -f(\text{Fe}) \\
N_{05} = N_9 + N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17} \\
-f_6 = -f(\text{Ce}) \\
N_{01} = N_{26} + N_{27} + 2N_{28} + 2N_{29} + N_{30} + N_{31} + N_{32} + N_{33} + N_{34} + N_{35} + N_{36} + N_{37} \\
f_{12} = 2f_2 - f_1 \\
-N_2 + N_3 + 7N_{14} + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} + N_{13} + 2N_{14} + 2N_{15} + 8N_{16} + 16N_{17} + N_{27} + 3N_{28} + 4N_{29} + 8N_{30} + 16N_{31} + 24N_{32} + N_{34} + 8N_{35} + 16N_{36} + 24N_{37} = 16N_{01} + 6N_{02} + 4N_{04} + 8N_{05} + 6N_{06} + 4N_{08} \\
(18)
\end{align*}
\]

The linear combination
\[
\begin{align*}
f_{12} + f_6 - 6f_3 - 4f_0 &= 0 \\
(1+1)f_1 + (-2)f_2 + (+6)f_3 + (+4)f_4 - f_0 &= 0 \\
(+1)f(H) + (-2)f(O) + (+6)f(SO_4) + (+4)f(\text{CO}_3) - \text{ChB} &= 0
\end{align*}
\]

involving \( K^* = 4 \) balances for electron-non-active elements: H, O, S, C \((f(SO_4) = f(S), f(\text{CO}_3) = f(C))\) gives the equation:
\[
2(N_9 + N_{10} + N_{11}) + 3(N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17}) + 4(N_{26} + N_{27} + 2N_{28} + 2N_{29} + N_{30} + N_{31} + N_{32}) + 3(N_{33} + N_{34} + N_{35} + N_{36} + N_{37}) = 2N_{05} + 4N_{01} \\
(20)
\]

Denoting atomic numbers: \( Z_{\text{Fe}} = 26, Z_{\text{Ce}} = 58 \), from equations: 16, 17 and 20, we obtain the balance
\[
Z_{\text{Fe}}f_3 + Z_{\text{Ce}}f_6 - (2f_2 - f_1) + f_6 - 6f_3 - 4f_4
\]

\[
(Z_{\text{Fe}} - 2)(N_9 + N_{10} + N_{11}) + (Z_{\text{Fe}} - 3)(N_{12} + N_{13} + N_{14} + 2N_{15} + N_{16} + N_{17}) + (Z_{\text{Ce}} - 4)(N_{26} + N_{27} + 2N_{28} + 2N_{29} + N_{30} + N_{31} + N_{32}) + (Z_{\text{Ce}} - 3)(N_{33} + N_{34} + N_{35} + N_{36} + N_{37}) = (Z_{\text{Fe}} - 2)N_{05} + (Z_{\text{Ce}} - 4)N_{01} \\
(21)
\]

Applying the relations:
\[
\begin{align*}
[K_5^{+} \cdot (V_0 + V)] &= 10^5, \quad \Pi_1, \quad C_{02}V_0 = 10^5 \cdot N_{01}/N_A, \quad \text{and CV} = 10^5 \cdot N_{05}/N_A
\end{align*}
\]
in eq. 21, we obtain GEB, written in terms of molar concentrations
\[
(Z_{\text{Fe}} - 2)[(\text{Fe}^{2+}) + [\text{FeOH}^{+}]+[\text{FeSO}_4]) + (Z_{\text{Fe}} - 3)[(\text{Fe}^{3+}) + [\text{FeOH}^{+}]+[\text{FeOH}_2^{-}]+[\text{FeOH}_2^{+}]+[\text{FeOH}_3^{+}]+2[\text{Fe}_2(\text{OH})_2^{+}] + [\text{Ce(SO}_4)] + [\text{Ce(OH}_3] + [\text{Ce(OH}_4] + [\text{Ce}_2(\text{OH})_2] + [\text{Ce}_2(\text{OH})_4] + [\text{Ce}_2(\text{OH})_6] + [\text{Ce}_2(\text{OH})_8]
\]

\[
-(Z_{\text{Fe}} - 2)C_{02}V_0 + (Z_{\text{Ce}} - 4)CV)/(V_0 + V) = 0 \\
(21a)
\]

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

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

\[
[\text{Fe}^{2+}] + [\text{FeOH}^{+}] + [\text{FeSO}_4] - ([\text{Ce}^{4+}] + [\text{CeOH}^{+}]+[\text{Ce}_2(\text{OH})_3] + 2[\text{Ce}_2(\text{OH})_5] + [\text{Ce}_2(\text{OH})_7] + [\text{Ce}_2(\text{OH})_9] + [\text{Ce}_2(\text{OH})_{11}] + [\text{Ce}_2(\text{OH})_{13}])
\]

\[
(C_{02}V_0 - CV)/(V_0 + V) = 0 \\
(23a)
\]

From eq. 18, considered as the primary form of Generalized Electron Balance (GEB), \( f_{12} = pr\)-GEB, we obtain the equation
\[
-(H^{+}) + [\text{OH}^{+}] + 7[\text{HSO}_4] + 8[\text{SO}_4^{2-}] + 4[\text{H}_2\text{CO}_3] + 5[\text{HCO}_3^{-}] + 6[\text{CO}_3^{2-}] + [\text{FeOH}^{+}] + 8[\text{FeSO}_4] + [\text{FeOH}_2^{-}] + 2[\text{Fe}_2(\text{OH})_2^{+}] + 2[\text{Fe}_2(\text{OH})_4^{+}] + 8[\text{FeSO}_4^{+}] + 16[\text{Fe}_2(\text{OH})_5^{-}] + \text{[CeOH}^{+}]+3[\text{Ce}_2(\text{OH})_3^{+}] +\]

4[Ce(OH)$_4^{2-}$] + 8[CeSO$_4^{4-}$] + 16[Ce(SO$_4$)$_3^{-2}$] + 24[Ce(SO$_4$)$_3^{-1}$] + [CeOH$^{-2}$] + 8[CeSO$_4^{4+}$] + 
16[Ce(SO$_4$)$_2^{-1}$] + 24[Ce(SO$_4$)$_3^{-3}$] - (16CV + 6(C$_0$V$_0 + C_1V) + 4(C$_0$V$_0 + C_2V))/(V$_0 + V)= 0 \quad (18a)

where, in addition to relations 22, we apply

$$C_1V = 10^{3.771}, \quad C_0V_0 = 10^{3.771}, \quad C_2V = 10^{3.771}, \quad C_0V_0 = 10^{3.771}$$ \quad (24)

From eq. 20 we have

$$2([Fe^{3+}]+[FeOH^{+}]+[FeSO_4^{2+}]) + 3([Fe^{2+}]+[FeOH^{+}]+[FeOH^{2+}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+[FeSO_4^{1+}] + [Fe(OH)_2^{+4}])+4\cdot([Fe^{4+}]+[FeOH^{+}]+2[Ce_2(OH)_4^{2+}]+[Ce_2(SO_4)_2^{2+}]+[Ce(SO_4)_2^{2+}]+[Ce(SO_4)_3^{2-}]+3-([Ce^{3+}]+[CeOH^{+}]+[CeSO_4^{3+}]) + [Ce(SO_4)_2^{2-}]+[Ce(SO_4)_3^{3-}] - (2C_0V_0 + 4CV)/(V_0 + V) = 0 \quad (20a)

The linear combination of equations: 16 (multiplied by 2), 17 (multiplied by 4) and 20 gives the next/shortest form of GEB

$$[Fe^{3+}]+[FeOH^{+}]+[FeSO_4^{2+}]+2[Ce_2(OH)_4^{2+}]+[FeSO_4^{1+}] + [Fe(OH)_2^{+4}]+4\cdot([Fe^{4+}]+[FeOH^{+}]+2[Ce_2(OH)_4^{2+}]+[Ce_2(SO_4)_2^{2+}]+[Ce(SO_4)_2^{2+}]+[Ce(SO_4)_3^{2-}]+3-([Ce^{3+}]+[CeOH^{+}]+[CeSO_4^{3+}]) + [Ce(SO_4)_2^{2-}]+[Ce(SO_4)_3^{3-}] = 0 \quad (25)

where oxidized forms of Fe and reduced forms of Ce are interrelated; molar concentrations: C$_2$ and C are not involved there explicitly.

For calculation purposes, related to the System III, the GEB, e.g. eq. 23a, is completed by charge and concentrations balances, obtained from equations 13-17 and relations 22, 24:

$$[H^+] - [OH^{-}] - [HSO_4^{-}]+2[SO_4^{2-}]-[HCO_3^{-}]-2[CO_3^{2-}]+2[Fe^{2+}]+[FeOH^{+}]+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^{+}]+5[Ce_2(OH)_4^{2+}]+4[Ce_2(OH)_4^{+4}]+2[CeSO_4^{2-}]-2[Ce(SO_4)_2^{+2}] + 3[Ce^{3+}]+2[CeOH^{+}]+[CeSO_4^{3+}]-[Ce(SO_4)_2^{+1}]-3[Ce(SO_4)_3^{+3}] = 0 \quad (13a)

[HSO_4^{-}]+[SO_4^{2-}]+[FeSO_4^{1+}]+[Fe_2(SO_4)_2^{2+}]+2[Fe_2(SO_4)_2^{+2}]+[CeSO_4^{2-}]+2[Ce(SO_4)_2^{+2}]+3[Ce(SO_4)_3^{+3}]+2[CeSO_4^{3+}]+2[Ce(SO_4)_2^{+2}]+3[Ce(SO_4)_3^{+3}]-
(C_0V_0 + C_0V_0 + 2CV + C_1V)/(V_0 + V) = 0 \quad (14a)

$$[H_2CO_3]+[HCO_3^{-}]+[CO_3^{2-}]-C_0V_0 + C_2V)/(V_0 + V) = 0 \quad (15a)

$$[Fe^{2+}]+[FeOH^{+}]+[FeSO_4^{2+}]+[Fe_2(SO_4)_2^{2+}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+[FeSO_4^{1+}]+[Fe(SO_4)_2^{+1}]-C_0V_0/\quad (V_0 + V) = 0 \quad (16a)

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

$$+[CeOH^{+}]+[CeSO_4^{3f}]+[Ce(SO_4)_2^{+1}]+[Ce(SO_4)_3^{+3}]-CV/(V_0 + V) = 0 \quad (17a)

6. The relations for equilibrium constants values

Concentrations of some species are interrelated in the set of independent expressions, where numerical values for the corresponding equilibrium constants are involved, and applied in the related algorithms.

$$[H^+][OH^{-}] = 10^{-14.0}, \quad [HSO_4^{-}]=10^{1.8}[H^+]([SO_4^{2-}]; \quad [H_2CO_3]=10^{16.4}[H^+]^2([CO_3^{-}]; \quad [HCO_3^{-}]=10^{10.1}[H^+]([CO_3^{-}]; \quad [Fe^{3f}]= [Fe^{2f}]\cdot 10^{4.5}[Fe^{2f}][OH^{-}]; \quad [FeOH^{+}]=10^{4.5}[Fe^{2f}][OH^{-}]; \quad [Fe^{2f}]=10^{11.0}[Fe^{3f}][OH^{-}];$$

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

$$[Mn^{2f}]=10^{5.4}(A^{-1} - 1.507) + 8pH; \quad [Mn^{2f}]=10^{4.5}(A^{-1} - 1.743) + 8pH; \quad [Mn^{3f}]=10^{6.0}(A^{-1} - 1.507);$$

$$[Mn^{2f}]=10^{4.2}[Mn^{3f}][OH^{-}]; \quad [Mn^{2f}]=10^{4.2}[Mn^{3f}][OH^{-}];$$

$$[Ce^{4f}]=10^{4.5}(A^{-1} - 1.507); \quad [Ce^{3f}]=10^{4.5}(A^{-1} - 1.507); \quad [Ce^{4f}][OH^{-}];$$

$$[Ce_2(OH)_4^{2f}]=10^{13.3}[Ce^{4f}][OH^{-}]; \quad [Ce_2(OH)_4^{+4}]=10^{13.3}[Ce^{4f}][OH^{-}];$$
\[ [\text{Ce}_2(\text{OH})_3]^{+5} = 10^{40.3}[\text{Ce}^{4+}]^2[\text{OH}^{-1}]^3; \quad [\text{Ce}_2(\text{OH})_4]^{+4} = 10^{53.7}[\text{Ce}^{4+}]^2[\text{OH}^{-1}]^4; \quad [\text{CeOH}]^{+2} = 10^{50.9}[\text{Ce}^{3+}][\text{OH}^{-1}]; \]

\[ [\text{CeSO}_4]^{+1} = 10^{4.3}[\text{Ce}^{3+}][\text{SO}_4^{-2}]^2; \quad [\text{Ce}^2][\text{SO}_4^{-2}]^2; \quad [\text{Ce}^2(\text{SO}_4)^{-3}]; \quad [\text{Ce}^2(\text{SO}_4)^{3-}]; \quad [\text{Ce}^3][\text{SO}_4^{-2}]^3. \]  

where

\[ A = 1/	heta_0, \quad \theta_0 = \frac{RT}{\Phi} \log 10; \quad A = 16.9 \text{ at } T = 298 \text{ K.} \]  

### 7.1. Fraction titrated

The results of simulated titrations, with measurable values: potential E and/or pH of the D+T system, are plotted as the functions E = E(V) and/or pH = pH(V). In some instances, it is more advantageous/reasonable to plot the graphs: E = E(\(\Phi\)) and/or pH = pH(\(\Phi\)), with the fraction titrated [25-28]

\[ \Phi = \frac{C_0V}{C_0V_0} \]  

(28)

where C_0 – concentration [mol/L] of the analyte A in D, C – concentration [mol/L] of reagent B in T; V_0 mL is the volume of D taken for titration, V is the current/total volume of T added into D from the start up to a given point/moment of the titration. The \(\Phi\) provides a kind of uniformity/normalization of the related plots, i.e., independency on \(V_0\) value.

For the Systems I and III, where FeSO_4 is the single analyte, eq. 28 can be rewritten as follows

\[ \Phi = \frac{C_0V}{C_0V_0} \]  

(28a)

where C_0 = C_{02}.

The fraction titrated \(\Phi\) (eq. 28) will be applied first to formulate the Generalized Equivalent Mass (GEM) concept.

### 8. Generalized equivalent mass (GEM)

The main task of a titration made for analytical purposes is the estimation of the equivalent volume, \(V_{eq}\), corresponding to the volume V of T, where the fraction titrated (eq. 28) assumes the value

\[ \Phi_{eq} = \frac{C_0V_{eq}}{C_0V_0} \]  

(29)

equal to the ratio p/q of small natural numbers p and q, \(\Phi_{eq} = p/q\). This ratio will be formulated on the basis of location of characteristic points on redox titration curves E = E(\(\Phi\)).

In contradistinction to visual titrations, where the end (e) volume \(V_e \equiv V_{eq}\) is registered [21,27], all instrumental titrations aim, in principle, to obtain the \(V_{eq}\) value on the basis of experimental data \{(V_j, y_j) | j=1,....,N\}, where \(y = \text{pH or E for potentiometric methods of analysis. Referring again to eq. 28, we have}

\[ C_0 \cdot V_0 = 10^2 \cdot \frac{m_A}{M_A} \]  

(30)

where \(m_A [\text{g}]\) and \(M_A [\text{g/mol}]\) denote mass and molar mass of analyte (A), respectively. From equations: 28 and 30, we get

\[ m_A = 10^{-2} \cdot C \cdot M_A \cdot \frac{Y}{\Phi} \]  

(31)

The value of the fraction in eq. 31, obtained from eq. 28,
is constant during the titration. Particularly, at the end (e) and equivalent (eq) points we have

\[ \frac{V}{\phi} = \frac{c_o \cdot v_e}{c} \]

\[(32)\]

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 of the titration, and

\[ \Phi_0 = \frac{c \cdot v_e}{c_T \cdot v_c} \]

\[(34)\]

is the \( F \)-value related to the end point. From equations 31 and 33, one obtains:

\[ m_A = 10^{-3} \cdot c \cdot v_e \cdot \frac{M_A}{\phi_e} \]

\[ m_A = 10^{-3} \cdot c \cdot v_{eq} \cdot \frac{M_A}{\phi_{eq}} \]

\[(a)\] and \[(b)\]

\[(35)\]

This does not mean, however, that we may choose between equations 35a and 35b, to calculate \( m_A \). Namely, eq. 35a cannot be applied for the evaluation of \( m_A \): \( V_e \) is known, but \( F_e \) is unknown; calculation of \( F_e \) needs prior knowledge of \( C_0 \) value. However, \( C_0 \) is unknown before the titration; otherwise, the titration would be purposeless. Also eq. 35b is useless: the ‘round’ \( F_{eq} \) value is known exactly, but \( V_{eq} \) is unknown; \( V_e \) (not \( V_{eq} \)) is determined in visual titrations.

Because the equations: 35a and 35b appear to be useless, the third, approximate formula for \( m_A \), has to be applied, namely:

\[ m'_A = 10^{-3} \cdot c \cdot v_e \cdot \frac{M_A}{\phi_{eq}} \]

\[ m''_A = 10^{-3} \cdot c \cdot v_{eq} \cdot R_{eq}^A \]

\[(36)\]

where \( F_{eq} \) is put for \( F_e \) in eq. 35a, and

\[ R_{eq}^A = \frac{M_A}{\phi_{eq}} \]

\[(37)\]

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

\[ \delta = \frac{m_A - m_A'}{m_A} = \frac{m_A'}{m_A} - 1 = \frac{v_e}{v_{eq}} - 1 = \frac{\phi_e}{\phi_{eq}} - 1 \]

\[(38)\]

The Generalized Equivalence Mass (GEM) concept was formulated (1979) by Michałowski [18,19,21,25], as the counterproposal to earlier (1978) IUPAC decision [29], see also [30].

7. Computer program for the System I

The calculations in GATES/GEB are realized according to iterative computer program. The exemplary computer program, related to the System I, is as follows.

```plaintext
global V Vmin Vstep Vmax V0 C C2 C02 C04 C05 H OH fi pH E
global Kw pKw A K logK
```
global HSO₄ SO₄ logHSO₄ logSO₄
global H₂CO₃ HCO₃ CO₃ logH₂CO₃ logHCO₃ logCO₃
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

\[
\begin{align*}
\text{pH} & = x(1); \\
E & = x(2); \\
\text{Mn}² & = 10.^{10^{-x(3)}}; \\
\text{Fe}² & = 10.^{10^{-x(4)}}; \\
\text{SO₄} & = 10.^{10^{-x(5)}}; \\
\text{H₂CO₃} & = 10.^{10^{-x(6)}}; \\
\text{H} & = 10.^{10^{-\text{pH}}}; \\
\text{pKw} & = 14; \\
\text{Kw} & = 10.^{10^{-14}}; \\
\text{OH} & = \text{Kw}/\text{H}; \\
A & = 16.9; \\
\text{ZFe} & = 26; \\
\text{ZMn} & = 25; \\
\text{Mn}⁷O₄ & = \text{Mn}² . 10.^{(5.\text{A} . (E-1.507)+8.\text{pH})}; \\
\text{Mn}⁶O₄ & = \text{Mn}² . 10.^{(4.\text{A} . (E-1.743)+8.\text{pH})}; \\
\text{Mn}³ & = \text{Mn}² . 10.^{(\text{A} . (E-1.509))}; \\
\text{Fe}³ & = \text{Fe}² . 10.^{(\text{A} . (E-0.771))}; \\
\text{HSO₄} & = 10.^{1.8}.\text{H}.\text{SO₄}; \\
\text{HCO₃} & = 10.^{(\text{pH}-6.3)}\text{H₂CO₃}. \\
\text{CO₃} & = 10^{(\text{pH}-10.1)}\text{HCO₃}. \\
\text{Fe}²OH & = 10.^{4.5}.\text{Fe}² . \text{OH}; \\
\text{Fe}²SO₄ & = 10.^{2.3}.\text{Fe}² . \text{SO₄}; \\
\text{Fe}³OH & = 10.^{11.0}.\text{Fe}³ . \text{OH}; \\
\end{align*}
\]
Fe_{3}OH_{2} = 10^{21.7} \cdot Fe_{3} \cdot OH \cdot 2; 
Fe_{3}2OH_{2} = 10^{25.1} \cdot Fe_{3} \cdot 2 \cdot OH \cdot 2; 
Fe_{3}SO_{4} = 10^{4.18} \cdot Fe_{3} \cdot SO_{4}; 
Fe_{3}SO_{42} = 10^{7.4} \cdot Fe_{3} \cdot SO_{4} \cdot 2; 
Mn_{2}OH = 10^{3.4} \cdot Mn_{2} \cdot OH; 
Mn_{2}SO_{4} = 10^{2.28} \cdot Mn_{2} \cdot SO_{4}; 
Mn_{3}OH = 10^{14.2} \cdot Mn_{3} \cdot OH; 
K = C \cdot V / (V_0 + V);

%Charge balance 
\[ F = (H \cdot OH + K \cdot HSO_4 - HCO_3 - 2 \cdot SO_4 - Mn_7O_4 + 2 \cdot Mn_6O_4 - 3 \cdot Mn_3 + 2 \cdot Mn_3OH + 2 \cdot Mn_2 + Mn_2OH + 2 \cdot Fe_2 + Fe_2OH + 3 \cdot Fe_3 + 2 \cdot Fe_3OH + Fe_3OH_2 + 4 \cdot Fe_32OH_2 + Fe_3SO_4 - Fe_3SO_42); \]

%Concentration balance of Mn 
(Mn_7O_4 + Mn_6O_4 + Mn_3 + Mn_3OH + Mn_2 + Mn_2OH + Mn_2SO_4 - C \cdot V / (V_0 + V));

%Concentration balance of Fe 
(Fe_2 + Fe_2OH + Fe_2SO_4 + Fe_3 + Fe_3OH + Fe_3OH_2 + 2 \cdot Fe_32OH_2 + 
+Fe_3SO_4 + Fe_3SO_42 - C_02 \cdot V_0 / (V_0 + V));

%Concentration balance of S 
(HSO_4 + SO_4 + Mn_2SO_4 + Fe_2SO_4 + Fe_3SO_4 + 2 \cdot Fe_3SO_42; 
-(C_02 + C_04) \cdot V_0 / (V_0 + V));

%Concentration balance of C 
(H_2CO_3 + HCO_3 + CO_3 - (C_2 \cdot V + C_05 \cdot V_0) / (V_0 + V));

%Electron balance 
((Z \cdot Mn - 7) \cdot Mn_7O_4 + (Z \cdot Mn - 6) \cdot Mn_6O_4 + (Z \cdot Mn - 3) \cdot (Mn_3 + Mn_3OH) - 
+(Z \cdot Mn - 2) \cdot (Mn_2 + Mn_2OH + Mn_2SO_4) + (Z \cdot Fe - 2) \cdot (Fe_2 + Fe_2OH + Fe_2SO_4) - 
+(Z \cdot Fe - 3) \cdot (Fe_3 + Fe_3OH + Fe_3OH_2 + Fe_32OH_2 + Fe_3SO_4 + Fe_3SO_42) + 
-((Z \cdot Fe - 2) \cdot C_02 \cdot V_0 + (Z \cdot Mn - 7) \cdot C \cdot V) / (V_0 + V));

logMn_2 = log10(Mn_2); 
logMn_2OH = log10(Mn_2OH); 
logMn_2SO_4 = log10(Mn_2SO_4); 
logMn_3 = log10(Mn_3); 
logMn_3OH = log10(Mn_3OH); 
logMn_6O_4 = log10(Mn_6O_4);
logMn7O4 = log10(Mn7O4);
logFe2 = log10(Fe2);
logFe2OH = log10(Fe2OH);
logFe2SO4 = log10(Fe2SO4);
logFe3 = log10(Fe3);
logFe3OH = log10(Fe3OH);
logFe3OH2 = log10(Fe3OH2);
logFe3SO4 = log10(Fe3SO4);
logFe3SO42 = log10(Fe3SO42);
logH2SO4 = log10(H2SO4);
logSO4 = log10(SO4);
logH2CO3 = log10(H2CO3);
logHCO3 = log10(HCO3);
logCO3 = log10(CO3);
logK = log10(K);

8. Graphical and numerical presentation of results

The results of calculations for the System I are presented graphically in Figures 1a-d, 2a-d (with E = E(Φ) and pH = pH(Φ) functions), and 3a,b, 4a,b (with speciation diagrams). Numerical data (Φ, E) from the vicinity of the jump in potential E-value (Fig. 1a) are collected in Table 1 [31]. The jump occurs here at Φ = Φ_{eq} = 0.2, named as equivalent (eq) point; note that 0.20000 ≡ \frac{2}{5} = 1 : 5. The coordinates of equivalent point are (Φ_{eq}, E_{eq}) = (0.20000, 1.034), with Φ_{eq} as the stoichiometric point of the reaction

\[ \text{MnO}_4^{-1} + 5\text{Fe}^{2+} + 8\text{H}^{+} = \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \] (39)

This reaction written in terms of predominating species (see Figures 3a,b) is as follows

\[ \text{MnO}_4^{-1} + 5\text{FeSO}_4 + 6\text{HSO}_4^{-1} + 2\text{H}^{+} = \text{MnSO}_4 + 5\text{Fe(SO}_4)_2^{-1} + 4\text{H}_2\text{O} \] (40)

No changes in slope on the pH = pH(Φ) curves occur at Φ_{eq} = 0.2 (Fig. 1b), although one would expect, at first glance, that MnO_4^{-1} may act, especially in reaction 39, like 'octopus' swallowing H^+ at Φ < 0.2, while the reaction 39 does not occur at Φ > 0.2. High value of the dynamic buffer capacity [32-34] in the D+T system is responsible for suppressing this effect. Analogous remark is related to the System III, represented by E = E(Φ) and pH = pH(Φ) relationships (Fig. 2), and speciation curves (Fig. 4).

Fig. 1. The (1a) E = E(Φ) and (1b) pH = pH(Φ) curves plotted for the System I at V_0 = 100, (C_{02}, V_0, C) = (0.01, 100, 0.02) and different C_{04} values [mol/L], indicated in Figures 1b, 1c and 1d (in enlarged scales), before and after Φ_{eq} = 0.2; C_2 = C_{05} = 0.
9. Formulation of the modified Gran methods

9.1. Preliminary 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

$$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$$

is expressed by the Nernst equation

$$E = E_0^* + \theta \cdot \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = E_0^* + \alpha \cdot \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

Table 1. The pairs of ($\Phi$, $E$) values for the System I, $(C_{02}, C_{04}, V_0, C) = (0.01, 1.0, 100, 0.02)$ in the close vicinity of $(\Phi_{eq}, E_{eq})$; $E$ in NHE scale.

<table>
<thead>
<tr>
<th>$\Phi$</th>
<th>$E$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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<td>0.19900</td>
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<tr>
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<td>0.20020</td>
<td>1.382</td>
</tr>
<tr>
<td>0.20200</td>
<td>1.442</td>
</tr>
</tbody>
</table>

Fig. 2. The (2a) $E = E(\Phi)$ and (2b) $pH = pH(\Phi)$ curves plotted for the System III at $V_0 = 100$, $(C_{02}, V_0, C, C_1) = (0.01, 100, 0.1, 1.0)$ and different $C_{04}$ values [mol/L], indicated in Figures 2b, 2c and 2d (in enlarged scales), before and after $\Phi_{eq} = 1.0$; $C_2 = C_{05} = 0$. 

9. Formulation of the modified Gran methods

9.1. Preliminary 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

$$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$$

is expressed by the Nernst equation

$$E = E_0^* + \theta \cdot \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = E_0^* + \alpha \cdot \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

(41)
where $\theta = a \cdot \ln 10$ is the real slope of indicator electrode; $\epsilon$ and $E_0^*$ values are assumed constant during the titration; the $E_0^*$ involves standard redox potential $E_0$ for reaction 41, potential of reference electrode, and liquid junction potential.

**Fig. 3.** Dynamic speciation diagrams for (3a) Fe-species, (3b) Mn-species in the System I; $(C_{02}, C_{04}) = (0.01, 0.02, 1.0)$, $C_2=C_05=0$, $V_0=100$.

**Fig. 4.** Dynamic speciation diagrams for (4a) Fe-species, (4b) Ce-species in the System III; $(C, C_1, C_{02}, C_{04}) = (0.1, 0.5, 0.02, 1.0)$, $C_2=C_05=0$, $V_0=100$. 
For further discussion, we collect first the equations for GEB related to two different D+T systems: System I and System III, with FeSO$_4$ (C$_{02}$) + H$_2$SO$_4$ (C$_{04}$) as D. The GEB expressed by eq. 11a, and rewritten as follows:

\[ [\text{Fe}^{2+}][\text{FeOH}^{+}] + [\text{FeSO}_4] - 5[\text{MnO}_4^{-}] + 4[\text{MnO}_4^{2-}] + [\text{Mn}^{3+}] + [\text{MnOH}^{2-}] \]

\[ = (C_{02}V_0 - 5CV)/(V_0 + V) \]  

(11b)

is applicable for the Systems I and II, whereas concentration balance for Fe in the System II is presented as follows:

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

\[ = (C_{02} + 2C_{03})V_0/(V_0 + V) \]  

(4b)

For the System I, we have C$_{03}$=0 in eq. 4b, i.e.,

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

\[ = C_0V_0/(V_0 + V) \]  

(4c)

In turn, for the System III we refer to equations 23a and 16a, rewritten analogously:

\[ [\text{Fe}^{2+}][\text{FeOH}^{+}] + [\text{FeSO}_4] - ([\text{Ce}^{4+}] + [\text{CeOH}^{3+}] + 2[\text{Ce}_2\text{(OH)}_4^{4+}] + [\text{CeSO}_4^{3-}] + [\text{Ce}(\text{SO}_4)_2^{-2}] = (C_{02}V_0 - CV)/(V_0 + V), \text{ and} \]  

(23b)

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

\[ = C_0V_0/(V_0 + V) \]  

(16b)

The latter one is identical with eq. 4c.

### 9.2. Derivation of formulas for the Systems I and III

From relations: CV = $\Phi$C$_{02}$V$_0$, and CV$_{eq}$ = $\Phi_{eq}$C$_{02}$V$_0$, we have

\[ \frac{V}{V_{eq}} = \frac{\Phi}{\Phi_{eq}} \]  

(43)

At low pH values (Figures 1b, 2b), on the basis of speciation diagrams (Figures 3, 4), the balances: 11b and 23b at $\Phi < \Phi_{eq}$ can be presented in the simplified forms:

\[ [\text{Fe}^{2+}] + [\text{FeSO}_4] = (C_{02}V_0 - 5CV)/(V_0 + V) \]  

(at $\Phi_{eq} < 0.2$, for the Systems I, II)  

(11c)

\[ [\text{Fe}^{2+}] + [\text{FeSO}_4] = (C_{02}V_0 - CV)/(V_0 + V) \]  

(at $\Phi_{eq} < 1.0$, for the System III)  

(23c)

At $\Phi_{eq} < 0.2$ for the System I (Fig. 2) and at $\Phi_{eq} < 1.0$ (Fig. 4) for the System III, the simplified balance for Fe can be applied

\[ [\text{Fe}^{2+}] + [\text{FeSO}_4] + [\text{Fe}^{3+}] + [\text{FeSO}_4^{3-}] + [\text{Fe}(\text{SO}_4)_2^{-1}] = C_0V_0/(V_0 + V) \]  

(4c)

Applying the appropriate formulas found in (26), from equations: 11c, 23c and 4c we get, by turns:

\[ [\text{Fe}^{2+}] \cdot b_2 = (C_{02}V_0 - 5CV)/(V_0 + V) \]  

(11d)

\[ [\text{Fe}^{2+}] \cdot b_2 = (C_{02}V_0 - CV)/(V_0 + V) \]  

(23d)

\[ [\text{Fe}^{2+}] \cdot b_2 + [\text{Fe}^{3+}] \cdot b_3 = C_0V_0/(V_0 + V) \]  

(4d)

where: $b_2 = 1 + 10^{2.3} \times [\text{SO}_4^{2-}]$, $b_3 = 1 + 10^{4.18} \times [\text{SO}_4^{2-}] + 10^{7.4} \times [\text{SO}_4^{2-}]^2$, i.e.,

\[ \frac{b_3}{b_2} = \frac{1 + 10^{4.18} \times [\text{SO}_4^{2-}] + 10^{7.4} \times [\text{SO}_4^{2-}]^2}{1 + 10^{2.3} \times [\text{SO}_4^{2-}]} \]  

(44)

From equations: 11d, 4d, 43 and $\Phi_{eq} = 0.2 = \frac{1}{5}$, we have

\[ \frac{b_3}{b_2} [\text{Fe}^{3+}] = \frac{1}{1 - 5\Phi} \quad \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{b_3}{b_2} \cdot \frac{s - \Phi}{1 - 5\Phi} = \frac{b_3}{b_2} \cdot \frac{V}{V_{eq} - V} \]  

(45)

whereas from equations: 23d, 4d, 43 and $\Phi_{eq} = 1$, we have
\[ 1 + \frac{b_2}{b_2} \cdot [\text{Fe}^{2+}] = \frac{1}{1 + \frac{b_2}{b_2} \cdot [\text{Fe}^{2+}] \cdot \Phi} = \frac{b_2}{b_2} \cdot \frac{V}{V_{eq} - V} \]  

(i.e., the expressions for the ratio \([\text{Fe}^{2+}]\) are identical in the Systems: I and III. In the System III, the value of (eq. 44) depends on \(H_2SO_4\) concentrations: \(C_{04}\) in D, and \(C_1\) in T, whereas in the System I, we have \(C_1 = 0\) in T. Then from equations: 42 and 45 (or 46), we get the relation

\[ E = E^0_i - a \cdot \ln \frac{b_2}{b_2} + a \cdot \ln V - a \cdot \ln (V_{eq} - V) \]  

valid for \(V < V_{eq}\).

The \(\theta = \ln \frac{b_2}{b_2}\) vs. \(\Phi\) relationships [10] are plotted for the Systems: I (Fig. 5a) and III (Fig. 5b). We see that in Fig. 5a, and in Fig. 5b. Then we can assume the relation

\[ \ln \frac{b_2}{b_2} = \alpha - \gamma \cdot \Phi = \alpha - \beta \cdot V \]  

where \(a, g\) and \(b = \frac{\gamma c}{C_{04} \cdot V_i}\) denote constant values for the given titration. Applying eq. 48 in eq. 47, we have

\[ E = \omega + a \cdot \beta \cdot V + a \cdot \ln V - a \cdot \ln (V_{eq} - V) \]  

where \(\omega = E^0_i - a \cdot \alpha\) is the new constant value, obtained from constant values introduced above. From eq. 49 we have, by turns,

\[ \frac{E - \omega}{a} = \beta \cdot V + \ln \frac{V}{V_{eq} - V} \Rightarrow E - \omega = \beta \ln a \cdot V + \log \frac{V}{V_{eq} - V} \Rightarrow \]

\[ \Omega = e^{-\frac{\omega}{a}} \cdot e^{-\beta \cdot V} \cdot (V_{eq} - V) \]  

where \(\delta = a \cdot \ln 10\), and

\[ \Omega = V \cdot 10^{-\frac{\omega}{a}} \]  

At high \(C_{04}\) value, the change of \(\frac{b_2}{b_2}\) value is relatively small (Figures 5a,b); \(b = 1.7 \times 10^{-3}\) at \(C_{04} = 1\) mol/L. Then the assumption \(\ln \frac{b_2}{b_2} = \text{const}\) can be applied below in the simplified model. Putting \(\beta = 0\) in eq. 50, we get

\[ \Omega = G_2 \cdot (V_{eq} - V) \]  

where \(G_2 = 10^{-\frac{\omega}{a}} = \text{const}\). Applying in eq. 50 the approximation \(e^{-\beta V} \cong 1 - \beta \cdot V\), valid for \(|\beta| \cdot V \ll 1\), we have, by turns

\[ \Omega = G_2 \cdot (1 - \beta \cdot V) \cdot (V_{eq} - V) \]

\[ \Omega = P \cdot V^2 - Q \cdot V + R \]  

where:
\[ P = G_2 \beta, \quad Q = G_2 (\beta \cdot V_{eq} + 1), \quad R = G_2 \cdot V_{eq} \]  \hspace{1cm} (54)

Eq. 53 rewritten in the form of regression equation

\[ \Omega_j = V_j \cdot 10^{-\frac{E_j}{n}} = P \cdot V_j^2 - Q \cdot V_j + R + \varepsilon_j \]  \hspace{1cm} (53a)

is the basis for calculation of values for parameters: \( P, Q, R \), determined according to the LSM. On the basis of relations 54, we get, by turns,

\[ \frac{R}{P} = \frac{V_{eq}}{\beta}, \quad \frac{Q}{R} = \frac{1}{V_{eq}}, \quad P \cdot V_{eq}^2 - Q \cdot V_{eq} + R = 0 \]

\[ V_{eq} = \frac{Q - Q^2 + P \cdot R}{2 \cdot P} \]  \hspace{1cm} (55)

Equations 53a and 55 are the basis for the modified Gran II method in its accurate version, denoted in [ACA606] as MG(II)A, which improves the results dramatically. Moreover, the error \( z \) of analysis is not affected significantly by the true \( \vartheta \) value for the slope of an indicator electrode.

**Fig. 5.** The \( q = \ln(b_3/b_2) \) vs. \( F \) relationships for the Systems: I (5a), at \((C, C_{02}) = (0.02, 0.01)\), and III (5b), plotted at \((C, C_1, C_{02}) = (0.1, 0.5, 0.01)\), \( V_0 = 100 \), \( C_2 = C_{05} = 0 \), and different \( C_{04} \) values indicated at the corresponding curves.

**9.3. Accurate model**

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. 49 we have

\[ E_{j+1} - E_j = a \cdot \beta \cdot (V_{j+1} - V_j) + a \cdot \ln \frac{V_{j+1}}{V_j} - a \cdot \ln \frac{V_{eq} - V_{j+1}}{V_{eq} - V_j} \]  \hspace{1cm} (56)

Applying in eq. 56 the identities:

\[ \frac{V_{j+1}}{V_j} = 1 + x_{ij}, \quad \frac{V_{eq} - V_{j+1}}{V_{eq} - V_j} = 1 - x_{ij} \]

where:
\[ x_{ij} = \frac{V_{i+1} - V_j}{v_i}, \quad x_{2j} = \frac{V_{i+1} - V_j}{v_{eq} - v_j} \quad (57) \]

we get

\[ E_{t+1} - E_t = a \cdot \beta \cdot (V_{i+1} - V_j) + a \cdot \ln(1 + x_{ij}) - a \cdot \ln(1 - x_{2j}) \quad (58) \]

Applying in eq. 52 the approximation [9-11,25,35] (see Fig. 6)

\[ \ln(1 + x_{ij}) \approx \left( \frac{1}{x_{ij} + \frac{1}{2}} \right)^{-1} \quad \text{and} \quad \ln(1 - x_{2j}) \approx \left( \frac{1}{x_{ij} - \frac{1}{2}} \right)^{-1} \quad (59) \]

we write

\[
\begin{align*}
\ln(1 + x_{ij}) - \ln(1 - x_{2j}) &= \left( \frac{1}{x_{ij} + \frac{1}{2}} \right)^{-1} + \left( \frac{1}{x_{ij} - \frac{1}{2}} \right)^{-1} \\
&= \left( \frac{4}{x_{ij} + x_{2j}} \right) - \frac{(V_{i+1} - V_j)v_{eq}}{(V_j - v_{eq} - V_j)} = (V_{j+1} - V_j) \cdot \left( \frac{2}{v_j} + \frac{1}{v_{eq} - v_j} \right) \\
&= \frac{V_j^i}{2} \\
\end{align*}
\]

where

\[ V_j^i = \frac{V_{j+1} + V_j}{2} \quad (61) \]

**Fig. 6.** 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) \( f_3(x) = x, \ x \in [0, 1] \).

Applying eq. 60b in eq. 58, we get the accurate model, written in terms of regression equation

\[ y_j^i = \frac{x_{ij} + x_{2j}}{V_{i+1} - V_j} = a \cdot \beta + a \cdot \left( \frac{1}{v_j} + \frac{1}{v_{eq} - v_j} \right) \quad (62) \]

The parameters: \( V_{eq}, a \) and \( \beta \) are obtained there according to an iterative computer program, by minimization of the sum of squares

\[ SS = \sum_i \left( a \cdot \beta + a \cdot \left( \frac{1}{v_j} + \frac{1}{v_{eq} - v_j} \right) - y_j^i \right)^2 \quad (63) \]

### 9.4. Approximate models (\( \beta = 0 \))

**Model 1.**

Putting \( \beta = 0 \) in eq. 62, we get, after transformation

\[ y_j^i = \frac{1}{V_j} \cdot \frac{V_{i+1} - V_j}{E_{i+1} - E_j} = G_1 \cdot (V_{eq} - V_j) \quad (64) \]

where
\[ G_1 = \frac{1}{\sigma V_{eq}} \]  

is a constant value, for the specific titration, see eq. 61. Denoting

\[ R = G_1 \cdot V_{eq} \]  

from eq. 58 we have the regression equation

\[ y_i^* = R - G_1 \cdot V_j^* + \epsilon_i \]  

The \( R \) and \( G_1 \) are determined there according to LSM:

\[
R = \frac{\sum y_i^2 - \sum y_i \sum V_j^*}{(N-2)\sum V_j^2 - (\sum V_j^*)^2}; \quad G_1 = \frac{1}{(N-1)\sum y_i^2 - (\sum y_i)^2}
\]  

and then we get

\[
V_{eq} = \frac{R - \sum y_i^2 \sum V_j^* - \sum y_i \sum V_j^*}{(N-1)\sum y_i V_j^* - (\sum V_j^*)^2}
\]

where \( \Sigma = \sum_{j=1}^{N-1} \) in equations 68, 69; \( N \) – number of exp. points \((V_j,E_j)\) \( j=1,\ldots,N \). The formulation applied here is the basis for the modified G(I) method in its simplified version, denoted as MG(IS) version [10]. The great advantage of MG(IS) over G(I) method results from application of formulas 59 instead of approximation \( \ln(1\pm x) \approx \pm x \) inherent in the G(I) method, see Fig. 6.

**Model 2.**

Referring again to eq. 52, we calculate the first and second derivatives of \( \Omega \) (eq. 51) [11]:

\[
\frac{d\Omega}{dv} = 10^{-\frac{E}{\sigma}} \cdot \left(1 - \ln10 \cdot \frac{\Delta E}{\sigma} \cdot \frac{dE}{dv}\right)
\]

\[
\frac{d^2\Omega}{dv^2} = 10^{-\frac{E}{\sigma}} \cdot \left[\ln10 \cdot \frac{\Delta E}{\sigma} \cdot \frac{dE}{dv} + 2 \cdot \frac{d^2E}{dv^2} \cdot \ln10 \cdot \frac{dE}{dv} \cdot \frac{d^2E}{dv}\right]
\]

Note that the first derivative of eq. 52 is \( \frac{d\Omega}{dv} = -G_2 = \text{const (at } \beta=0\text{)}; \) then \( \frac{d^2\Omega}{dv^2} = 0 \). Zeroing the second derivative (eq. 71) gives

\[ \theta = \ln10 \cdot \frac{V_j^2}{V_{j+1}^2 + 2 \cdot \frac{\Delta E}{\sigma}} \]

The first and second derivatives on the right side of Eq. 71 can be approximated by differential quotients

\[ \theta \approx \ln10 \cdot \frac{V_j^2}{V_{j+1}^2 + 2 \cdot \frac{\Delta E}{\sigma}} \]

where

\[
\frac{\Delta^R}{\Delta V} = \frac{\Delta^R}{\Delta V^2}
\]

For the set of experimental points \( \{(V_j,E_j)\} \ j = 1,\ldots,N-1 \}, we have: \( \Delta V = V_{j+1} - V_j \), \( \Delta E = E_{j+1} - E_j \). Both differential quotients: \( \frac{\Delta E}{\Delta V} \) and \( \frac{\Delta^R}{\Delta V^2} \) are put at \( V_j^* \) (eq. 61). Then the \( J = J(V_j) \) values were calculated from the formula 72a. The formulas presented here are the basis for the MG(II)B method [11]. An alternative is here the MG(II)C method [11], based on the Lagrange polynomial interpolation method.
The interrelations between G(I), G(II) and different modifications of these methods are collected in [11].

9.5. Derivation of formulas for the System II

Referring to the System II, one can state/assume that the composition of the titrand D can be affected here by partial oxidation of the iron(+2) species by oxygen from air, as in the case of natural waters.

As stated above, eq. 11b and eq. 11d, as its simplified form, are valid also for the System II. At $\Phi < 0.2$, the balance 4b can be written as follows

$$[\text{Fe}^{+2}] \cdot b_2 + [\text{Fe}^{+3}] \cdot b_3 = (C_{02} + C_{03}) \cdot \frac{V_a}{V_{\gamma} + V}$$  \hspace{1cm} (73)

Then from equations 11d and 73 we get, by turns,

$$1 + \frac{[\text{Fe}^{+2}] \cdot b_2 + [\text{Fe}^{+3}] \cdot b_3}{[\text{Fe}^{+2}] \cdot b_2 + [\text{Fe}^{+3}] \cdot b_3} = \frac{(C_{02} + C_{03}) \cdot V_0}{C_{02} \cdot V_0 + C_{03} \cdot V_0}$$

$$\frac{[\text{Fe}^{+2}] \cdot b_2 + [\text{Fe}^{+3}] \cdot b_3}{[\text{Fe}^{+2}] \cdot b_2 + [\text{Fe}^{+3}] \cdot b_3} = \frac{C_{02} \cdot V_0}{C_{02} \cdot V_0} = \frac{C_{03} \cdot V_0}{C_{03} \cdot V_0} = \frac{C_{02} \cdot V_0}{C_{03} \cdot V_0}$$

At $C_{03}=0$, eq. 74 is transformed into equations 45, 46. From equations 42 and 74 we have

$$E = E_0 - a \cdot \ln \frac{b_2}{b_2} + a \cdot \ln \left(\frac{C_{02} \cdot V_{eq} + V}{C_{02} \cdot V_{eq} + V_0}\right) - a \cdot \ln \left(\frac{V_{eq} + V}{V_{eq} + V_0}\right)$$  \hspace{1cm} (75)

Assuming $\ln \frac{b_2}{b_2} = \text{const}$, i.e., $\beta = 0$ in eq. 48, and applying eq. 75 for two consecutive points $(V_j, E_j)$ and $(V_{j+1}, E_{j+1})$ referred to potentiometric titration of D with T in the System II, we have

$$E_{j+1} - E_j = a \cdot \ln \left(\frac{C_{02} \cdot V_{eq} + V_{j+1}}{C_{02} \cdot V_{eq} + V_{j}}\right) - a \cdot \ln \left(\frac{V_{eq} + V_j}{V_{eq} + V_{j+1}}\right)$$  \hspace{1cm} (76)

Denoting

$$x_{j1} = \frac{V_{j+1} - V_j}{C_{02} \cdot V_{eq} + V_j}, \quad x_{j2} = \frac{V_{eq} - V_j}{V_{eq} - V_j}$$  \hspace{1cm} (77)

from eq. 76 we get

$$E_{j+1} - E_j = a \cdot \ln (1 + x_{j1}) - a \cdot \ln (1 - x_{j1})$$  \hspace{1cm} (78)

Applying the approximations 59 for 77, after transformations of eq. 76 we get, by turns,

$$E_{j=1} - E_j = a \cdot \left(\frac{1}{v_{j+1} - V_j} + \frac{1}{V_{eq} - V_j}\right)$$

$$x_{j1} = \frac{x_{j1} \cdot V_{eq} + V_{j}}{C_{02} \cdot V_{eq} + V_{j} + C_{03} \cdot V_{eq} + V_{j}}$$

$$u_j = \frac{V_{j+1} - V_j}{E_{j+1} - E_j} = \frac{C_{02} \cdot V_{eq} + C_{03} \cdot V_{eq}}{a \cdot V_{eq} + C_{02} \cdot V_{eq} + C_{03} \cdot V_{eq}}$$

$$u_j = P + Q \cdot V_{j+1} - R \cdot V_j^2 + \epsilon_j$$  \hspace{1cm} (79)

where $\Phi_{eq} = \frac{1}{5}$. 
\[
P = \frac{c_{02} - c_{03} \cdot V_{j}}{a \cdot (c_{02} + c_{03})} ; \quad Q = \frac{c_{02} - c_{03}}{a \cdot (c_{02} + c_{03})} ; \quad R = \frac{5 \cdot c}{a \cdot (c_{02} + c_{03})} V_{j}
\] (80)

and \( \epsilon_{j} \) is the difference between the \( u_{j} \) value found from measurements and the \( u_{j}(V_{j}) \) value found at \( V = V_{j} \) from the model assumed. Then we calculate [9]

\[
P = \left( \frac{V_{j}}{5c} \right)^{2} \cdot c_{02} \cdot c_{03} ; \quad Q = \frac{V_{j}}{5c} \cdot (c_{02} - c_{03})
\] (81)

(a) \[
c_{02} = \frac{5c}{2V_{j}} \left[ \sqrt{\left( \frac{P}{R} \right)^{2} + 4 \cdot \frac{P}{R} + 1} \right] ; \quad c_{03} = \frac{5c}{2V_{j}} \left[ \sqrt{\left( \frac{Q}{R} \right)^{2} + 4 \cdot \frac{Q}{R} - 1} \right]
\] (b)

One should note that the factor \( a = \frac{6}{\ln 15} \) in eq. 75 and in the formulas for \( P, Q, R \) (equations 80) does not enter the expression for \( \frac{P}{R} \) and \( \frac{Q}{R} \) (equations 81), i.e., the values for \( c_{02} \) and \( c_{03} \) (equations 82a,b) are not biased by the \( a \)-value that may differ, to some extent, from the Nernstian value, \( a_0 = \frac{RT}{F} \) (see eq. 27), as for electrodes commonly applied in potentiometric titrations.

Compact formulas needed for calculation of the \( c_{02} \) and \( c_{03} \) values on the basis of eq. 76 are obtained if equal, consecutive portions \( V_{j+1} - V_{j} = \Delta V \) of the titrant are added, i.e., \( V_{j} = j \cdot \Delta V, j=1,\ldots, N, \quad V_{j}^{\prime} = \frac{2j+1}{2} \cdot \Delta V \), and:

\[
\Sigma_{j=1}^{N} V_{j}^{k} = \left( \frac{\Delta V}{2} \right)^{k} \cdot \left[ \Sigma_{j=1}^{N} (2j + 1)^{k} \right] = \left( \frac{\Delta V}{2} \right)^{k} \cdot \left[ \Sigma_{j=1}^{N} (2j + 1)^{k} - 1 \right]
\]

The following formulas [9] are applicable here:

\[
\Sigma_{j=1}^{N} (2j - 1) = N^{2} ; \quad \Sigma_{j=1}^{N} (2j - 1)^{2} = \frac{1}{3} \cdot N(4N^{2} - 1) ; \quad \Sigma_{j=1}^{N} (2j - 1)^{3} = N^{2}(2N^{2} - 1) ;
\]

\[
\Sigma_{j=1}^{N} (2j - 1)^{4} = \frac{1}{15} \cdot N(4N^{2} - 1)(12N^{2} - 7)
\]

Then we have:

\[
P = \left( \frac{\Delta V}{2} \right)^{2} \cdot \left[ \Sigma_{j=1}^{N} u_{j} \Sigma_{j=1}^{N} (2j+1) \Sigma_{j=1}^{N} (2j+1)^{2} \Sigma_{j=1}^{N} (2j+1)^{3} \right]
\]

\[
Q = \frac{\Delta V}{2} \cdot \left[ \Sigma_{j=1}^{N} u_{j} \Sigma_{j=1}^{N} (2j+1) \Sigma_{j=1}^{N} (2j+1)^{2} \Sigma_{j=1}^{N} (2j+1)^{3} \right]
\]

10. Application of Gran methods for calibration purposes

Calibration of redox indicator electrodes (RIEs) is of primary importance in potentiometric measurements performed in redox systems. The difficulties in calibration of RIEs were probably the main reason for generating the opinion on inapplicability of the Gran II (G(II)) method for determination of equivalence volume (\( V_{eq} \)) in redox titrations. This problem has been exposed [10], where inaccuracy of the results obtained according to G
(II) method at greater discrepancies between true (correct, J) and pre-assumed (J_<sub>c</sub>) slope values, |J - J_<sub>c</sub>| for RIEs has been proved [10]. It was also stated that the error in V<sub>eq</sub> can be substantially decreased, even at greater |J - J_<sub>c</sub>| values, if the modified Gran II method in its accurate version (MG(II)A) proposed in [10] is applied; the MG (II)A method improves the results dramatically (Fig. 7). The error z is not affected significantly by the true 9-value of an indicator electrode.

Fig. 7. The relationships between relative error e [%] in V<sub>eq</sub> determination vs J [mV] plotted for G(II) and MG (II)A methods, at J_<sub>c</sub> = 56 mV value pre-assumed in calculations [11].

11. Final comments

It is stated that the linearizing approaches, inherent in original G(I) and G(II) methods, may provide inaccurate results of analyses. It were stated that the original Gran methods, particularly G(I) method [1], do not provide accurate results for V<sub>eq</sub>; the errors involved in G(I) may exceed tens percents, as indicated in [12]. Far more accurate results of analysis are obtainable according to the modified methods proposed by Michałowski in a series of papers [9-12,25], after recalling to the physicochemical nature of the system tested.

Also the original G(II) [3] method may not provide accurate results in the titrations; the matter lies in the divergence (ranging several percents [9]) between true and Nernstian slopes of the indicator electrode and in some difficulties encountered in calibration of this electrode.

In contradistinction to the G(II) method, the G(I) method offers the possibility to perform the potentiometric titrations without prior knowledge of 9 – provided that 9 is constant within defined V-range covered in the Gran methods, where the validity of assumption 9 = 9(V) = const is increased – in contradistinction to the methods based on the inflection point location; a dramatic change of the analyte concentration occurs in the vicinity of this point. Such advantages of G(I) method were successfully exploited in the modified G(I) methods [9-12,25], thereafter referred to as simplified (MG(I)S) and accurate (MG(I)A) methods [10].

The results of calculations related to redox systems were obtained according to GATES/GEB principles, with use of the iterative computer program MATLAB and the generator of pseudo-random numbers [36]; these results were confirmed experimentally in [10,11].

The Generalized approach to electrolytic systems (GATES) [13] with the generalized electron balance (GEB) involved as GATES/GEB, is adaptable for resolution of thermodynamic (equilibrium and metastable) redox systems of any degree of complexity; none simplifying assumptions are needed [10]. Application of
GATES provides the reference levels for real analytical systems, where some effects involved with kinetics and transportation (diffusion) phenomena occurred at the electrodes. The GATES makes possible to exhibit some important details, of qualitative and quantitative nature, invisible in real experiment, e.g. speciation. Reliability of physicochemical data (standard potentials, equilibrium constants of complexes, etc.) values is needed for this purpose. This requirement is fulfilled, among others, for 1° manganometric and 2° cerometric titrations of ferrous ions, where equilibria are established rapidly in the bulk solution. This way, we provide an approach to a more general problem involved with optimization a priori in redox systems, realized according to GATES principle.

The GATES approach is based on mathematical foundations, expressed by a system of nonlinear algebraic equations, not on a “fragile” chemical reaction notation, based on stoichiometry. Within GATES, the stoichiometry concept, as a resultant of all particular (stoichiometric, in principle) chemical reactions occurred in a dynamic system (as titration is) is not applied. Among others, the generalized equivalence mass (GEM) concept, based on GATES, is not involved with the stoichiometry concept. The stoichiometry is only a redundant concept within GATES and then formulation of reaction notation can be considered only as a kind of intellectual/didactic occupation, that can be made after presentation of the related curves obtained from calculations based on GATES.

The GEB (as Approaches I and II to GEB), GATES, GEM and all modifications of the Gran methods were discovered/suggested/formulated by Michałowski [9-12,25], and extended on different acid-base systems, involved also with total alkalinity [28,36,37], also with fulvic acids involved [38], and carbonate alkalinity [39], in particular.

REFERENCES


