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

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Research

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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°) $FeSO_4$ and (2°) $FeSO_4 + Fe_2(SO_4)_3$ mixture with $KMnO_4$ or $Ce(SO_4)_2$ 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.

Notations and acronyms: D – titrand (solution titrated); E – voltage [V]; GATES – Generalized approach to electrolytic systems; GEB – Generalized electron balance; LSM – least squares method; T – titrant; V_0 – volume [mL] of D; V – volume of T added into D from the start up to a given point of titration: $T(V) \Rightarrow D(V_0)$.

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 : $KMnO_4$ (C) + CO_2 (C_2) $\Rightarrow$ $FeSO_4$ (C_{02}) + H_2SO_4 (C_{04}) + CO_2 (C_{05}) ,

System II : $KMnO_4$ (C) + CO_2 (C_2) $\Rightarrow$ $FeSO_4$ (C_{02}) + $Fe_2(SO_4)_3$ (C_{03}) + H_2SO_4 (C_{04}) + CO_2 (C_{05}) ,

System III : $Ce(SO_4)_2$ (C) + H_2SO_4 (C_1) + CO_2 (C_2) $\Rightarrow$ $FeSO_4$ (C_{02}) + H_2SO_4 (C_{04}) + CO_2 (C_{05}) ,

where C, C_1, C_2 and 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 $X_i^{z_i}$ is formed.

We refer here to aqueous electrolytic systems, where the species $X_i^{z_i}$ exist as hydrates $X_i^{z_i} \cdot n_{iW}$, i=1,…, I; $z_i = 0, \pm1, \pm2, \ldots$ is a charge, expressed in elementary charge units, e = F/N_A (F = 96485 C·mol^{-1} – Faraday's constant, $N_A = 6.022\cdot10^{23}$ mol^{-1} – Avogadro's number), $n_i = n_{iW} = n_iH_2O \geq 0$ is a mean number of water (W=H_2O) molecules attached to $X_i^{z_i}$; 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,…,J) represented by molecules, and N_i – for the species $X_i^{z_i} \cdot n_{iW}$ (ions and molecules) of i-th kind (i = 1,…,I). The mono- or two-phase electrolytic system thus obtained involves N_1 molecules of H_2O and N_i species of i-th kind, $X_i^{z_i} \cdot n_{iW}$ (i=2, 3,…,I), specified briefly as $X_i^{z_i}$ (N_i, n_i), where $n_i \equiv n_{iW} \equiv n_iH_2O$. For ordering purposes, we write: H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3),…, where $z_2 = 1$, $z_3 = -1$,… .

The System II involves the non-redox subsystems:

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

(II.2) D(V_0) subsystem, composed of $FeSO_4\cdot7H_2O$ (N_{04}) + $Fe_2(SO_4)_3\cdot xH_2O$ (N_{05}) + H_2SO_4 (N_{06}) + H_2O (N_{07}) + CO_2 (N_{08}).

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 $Ce(SO_4)_2\cdot4H_2O$ (N_{01}) + H_2SO_4 (N_{02}) + H_2O (N_{03}) + CO_2 (N_{04}) ;

(III.2) D(V_0) subsystem, composed of $FeSO_4\cdot7H_2O$ (N_{05}) + H_2SO_4 (N_{06}) + H_2O (N_{07}) + CO_2 (N_{08}).

The common list of species, that will be applied/selected to particular Systems (I, II, III), is as follows: 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}); Ce^{+4} (N_{26}, n_{26}), $CeOH^{+3}$ (N_{27}, n_{27}), $Ce_2(OH)_3^{+5}$ (N_{28}, n_{28}), $Ce_2(OH)_4^{+4}$ (N_{29}, n_{29}), $CeSO_4^{+2}$ (N_{30}, n_{30}), $Ce(SO_4)_2$ (N_{31}, n_{31}), $Ce(SO_4)_3^{-2}$ (N_{32}, n_{32}), Ce^{+3} (N_{33}, n_{33}), $CeOH^{+2}$ (N_{34}, n_{34}), $CeSO_4^{+1}$ (N_{35}, n_{35}), $Ce(SO_4)_2^{-1}$ (N_{36}, n_{36}), $Ce(SO_4)_3^{-3}$ (N_{37}, n_{37}).

The species, with the related ordinal numbers, will be applied in the balances, formulated below. Molar concentrations [mol/L] of the species $X_i^{z_i} \cdot n_{iW}$ are denoted as $[X_i^{z_i}]$, 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) □ D(V-$_0$-), 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 = ChB, and elemental balances: $f_1 = f(\text{H})$ for E_1 = H (hydrogen) and $f_2 = f(\text{O})$ for E_2 = O (oxygen),… ; other elemental or core balances are denoted as $f_k = f(Y_k)$, $Y_k = E_k$ or *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., SO_4^{-2} is a core within the set of sulfate species: $HSO_4^{-1} \cdot n_4H_2O$, $SO_4^{-2} \cdot n_5H_2O$, $FeSO_4 \cdot n_{11}H_2O$ 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., $Ce(SO_4)_2 \cdot 4H_2O$ is dissolved in H_2SO_4 solution, not in water.

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

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

for elements with negative oxidation numbers, or

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

for elements with positive oxidation numbers, k ∊ 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 = ChB

$N_2 - N_3 - N_4 - 2N_5 - N_7 - 2N_8 + 2N_9 + N_{10} + 3N_{12} + 2N_{13} + N_{14} + 4N_{15} + N_{16} - N_{17} + N_{18} - N_{19} - 2N_{20} +$
$3N_{21} + 2N_{22} + 2N_{23} + N_{24} = 0$ (1)

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

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_9n_9 +$
$N_{10}(1+2n_{10}) + 2N_{11}n_{11} + 2N_{12}n_{12} + N_{13}(1+2n_{13}) + N_{14}(2+2n_{14}) + N_{15}(2+2n_{15}) + 2N_{16}n_{16} + 2N_{17}n_{17} +$
$2N_{18}n_{18} + 2N_{19}n_{19} + 2N_{20}n_{20} + 2N_{21}n_{21} + N_{22}(1+2n_{22}) + 2N_{23}n_{23} + N_{24}(1+2n_{24}) + 2N_{25}n_{25}$
$= 2N_{02} + 14N_{04} + 2xN_{05} + 2N_{06} + 2N_{07}$

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

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

$-f_3 = -f(\mathrm{SO_4})$

$N_{04} + 3N_{05} + N_{06} = N_4 + N_5 + N_{11} + N_{16} + 2N_{17} + N_{25}$ (2)

$-f_4 = -f(\mathrm{CO_3})$

$N_{03} + N_{08} = N_6 + N_7 + N_8$ (3)

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

$N_{04} + 2N_{05} = N_9 + N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + 2N_{15-} + N_{16} + N_{17}$ (4)

$-f_6 = -f(\mathrm{K})$

$N_{01} = N_{18}$ (5)

$-f_7 = -f(\mathrm{Mn})$

$N_{01} = N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25}$ (6)

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

$\underline{-N_2 + N_3 + 7N_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} + N_{13} + 2N_{14} + 2N_{15} + 8N_{16} + 16N_{17} +}$
$8N_{19} + 8N_{20} + N_{22} + N_{24} + 8N_{25} = 8N_{01} + 4N_{03} + 8N_{04} + 24N_{05} + 6N_{06} + 4N_{08}$ (7)

$2\cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4 - f_6 = 0 \quad \Leftrightarrow \quad (+1)\cdot f_1 + (-2)\cdot f_2 + (+6)\cdot f_3 + (+4)\cdot f_4 + (+1)\cdot f_6 - f_0 = 0 \quad \Leftrightarrow$
$(+1)\cdot f(\mathrm{H}) + (-2)\cdot f(\mathrm{O}) + (+6)\cdot f(\mathrm{SO_4}) + (+4)\cdot f(\mathrm{CO_3}) + (+1)\cdot f(\mathrm{K}) - \mathrm{ChB} = 0$ (8)

$2(N_9+N_{10}+N_{11}) + 3(N_{12}+N_{13}+N_{14}+2N_{15}+N_{16}+N_{17}) + 7N_{19} + 6N_{20} + 3(N_{21}+N_{22}) + 2(N_{23}+N_{24}+N_{25})$
$= 7N_{01} + 2N_{04} + 6N_{05}$ (9)

Denoting the atomic numbers: $Z_{Fe} = 26$, $Z_{Mn} = 25$, from equations: 4, 6 and 9, we obtain the balance

$Z_{Fe}\cdot f_5 + Z_{Mn}\cdot f_7 - (2\cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4 - f_6)$

$(Z_{Fe}-2)(N_9+N_{10}+N_{11}) + (Z_{Fe}-3)(N_{12}+N_{13}+N_{14}+2N_{15}+N_{16}+N_{17}) + (Z_{Mn}-7)N_{19} + (Z_{Mn}-6)N_{20} +$
$(Z_{Mn}-3)(N_{21}+N_{22}) + (Z_{Mn}-2)(N_{23}+N_{24}+N_{25}) = (Z_{Fe}-2)N_{04} + 2(Z_{Fe}-3)N_{05} + (Z_{Mn}-7)N_{01}$ (10)

Next, we can apply the combination of equations 4, 6 and 10, giving the shortest form of GEB

$3f_5 + 2f_7 - (2f_2 - f_1 + f_0 - 6f_3 - 4f_4 - f_6) = 0$

$(N_9+N_{10}+N_{11}) - (5N_{19} + 4N_{20} + N_{21}+N_{22}) = N_{04} - 5N_{01}$ (11)

Applying the relations:

$[X_i^{z_i}]\cdot(V_0+V) = 10^3\cdot\frac{N_i}{N_A}$, $CV = 10^3\cdot N_{01}/N_A$, $C_2V = 10^3\cdot N_{03}/N_A$, $C_{02}V_0 = 10^3\cdot N_{04}/N_A$, $C_{03}V_0 = 10^3\cdot N_{05}/N_A$,
$C_{04}V_0 = 10^3\cdot N_{06}/N_A$, $C_{05}V_0 = 10^3\cdot N_{08}/N_A$ (12)

in the balances derived above, we have the optional/equivalent equations for GEB. From eq. 7, considered as the *pr*imary form of Generalized Electron Balance (GEB), f_{12} = *pr*-GEB, we obtain the equation

$– [H^{+1}] + [OH^{-1}] + 7[HSO_4^{-1}] + 8[SO_4^{-2}] + 4[H_2CO_3] + 5[HCO_3^{-1}] + 6[CO_3^{-2}] + [FeOH^{+1}] +$
$8[FeSO_4] + [FeOH^{+2}] + 2[Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] + 8[FeSO_4^{+1}] + 16[Fe(SO_4)_2^{-1}] +$
$8[MnO_4^{-1}] + 8[MnO_4^{-2}] + [MnOH^{+2}] + [MnOH^{+1}] + 8[MnSO_4]$
$– (8CV + 4C_2V + 8C_{02}V_0 + 24C_{03}V_0 + 6C_{04\text{-}}V_0 + 4C_{05}V_0)/(V_0+V) = 0$ (7a)

Optionally, we have alternative forms of GEB for the System II:

$2([Fe^{+2}]+[FeOH^{+1}]+[FeSO_4]) + 3([Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}] +2[Fe_2(OH)_2^{+4}]+[FeSO_4^{+1}]+$
$[Fe(SO_4)_2^{-1}]) + 7[MnO_4^{-1}] + 6[MnO_4^{-2}] + 3([Mn^{+3}]+[MnOH^{+2}])$
$+ 2([Mn^{+2}]+[MnOH^{+1}]+[MnSO_4]) – (2C_0V_0 +7CV)/(V_0+V) = 0$ (9a)

$(Z_{Fe}–2)([Fe^{+2}]+[FeOH^{+1}]+[FeSO_4]) + (Z_{Fe}–3)([Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}]+[Fe(SO_{4\text{-}})_2^{-1}]) + (Z_{Mn}–7)[MnO_4^{-1}] + (Z_{Mn}–6)[MnO_4^{-2}] + (Z_{Mn}–3)([Mn^{+3}]+[MnOH^{+2}]) +$
$(Z_{Mn}–2)([Mn^{+2}]+[MnOH^{+1}]+[MnSO_4]) – ((Z_{Fe}–2)C_0V_0 + (Z_{Mn}–7)CV)/(V_0+V) = 0$ (10a)

$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4] – (5[MnO_4^{-1}] + 4[MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}])$
$– (C_0V_0 – 5CV)/(V_0+V) = 0$ (11a)

In other words, the GEB can be chosen arbitrarily from the set of equivalent equations: 7a, 9a, 10a, or 11a. The eq. 11a, as one of them, is completed by charge and concentration balances:

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

$[HSO_4^{-1}] + [SO_4^{-2}] + [FeSO_4] + [FeSO_4^{+1}] + 2[Fe(SO_4)_2^{-1}] + [MnSO_4] – (C_{02}+3C_{03}+C_{04})V_0/(V_0+V) = 0$
(2a)

$[H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] – (C_{05}V_0+C_2V)/(V_0+V) = 0$ (3a)

$[Fe^{+2}] + [FeOH^{+1}] + [FeSO_4] + [Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}]_{-} +$
$[FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}] – (C_{02}+2C_{03})V_0/(V_0+V) = 0$ (4a)

$[K^{+1}] = CV/(V_0+V)$ (5a)

$[MnO_4^{-1}] + [MnO_4^{-2}] + [Mn^{+3}] + [MnOH^{+2}] + [Mn^{+2}] + [MnOH^{+1}] + [MnSO_4] – CV/(V_0+V) = 0$ (6a)

The relation (5a), where only one species is involved, is considered as equality, not equation.

5. Formulation of balances for the System III

The balances are as follows:

f_0 = ChB

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

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + N_4(1+2n_4) + 2N_5n_5 + N_6(2+2n_6) + N_7(1+2n_7) + 2N_8n_8 + 2N_9n_9 +$
$N_{10}(1+2n_{10}) + 2N_{11}n_{11} + 2N_{12}n_{12} + N_{13}(1+2n_{13}) + N_{14}(2+2n_{14}) + N_{15}(2+2n_{15}) + 2N_{16}n_{16} + 2N_{17}n_{17} +$
$2N_{26}n_{26} + N_{27}(1+2n_{27}) + N_{28}(3+2n_{28}) + N_{29}(4+2n_{29}) + 2N_{30}n_{30} + 2N_{31}n_{31} + 2N_{32}n_{32} + 2N_{33}n_{33} +$
$N_{34}(1+2n_{34}) + 2N_{35}n_{35} + 2N_{36}n_{36} + 2N_{37}n_{37} = 8N_{01} + 2N_{02} + 2N_{03} + 14N_{05} + 2N_{06} + 2N_{07}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4(4+n_4) + N_5(4+n_5) + N_6(3+n_6) + N_7(3+n_7) + N_8(3+n_8) + N_9n_9 + N_{10}(1+n_{10\text{-}}) +$
$N_{11}(4+n_{11}) + N_{12}n_{12} + N_{13}(1+n_{13}) + N_{14}(2+n_{14}) + N_{15}(2+n_{15}) + N_{16}(4+n_{16}) + N_{17}(8+n_{17}) + N_{26}n_{26} +$
$N_{27}(1+n_{27}) + N_{28}(3+n_{28}) + N_{29}(4+n_{29}) + N_{30}(4+n_{30}) + N_{31}(8+n_{31}) + N_{32}(12+n_{32}) + N_{33}n_{33} + N_{34}(1+n_{34}) +$

$N_{35}(4+n_{35}) + N_{36}(8+n_{36}) + N_{37}(12+n_{37}) = 12N_{01} + 4N_{02} + N_{03} + 2N_{04} + 11N_{05} + 4N_{06} + N_{07} + 2N_{08}$

$-f_3 = -f(SO_4)$

$$2N_{01} + N_{02} + N_{05} + N_{06} = N_4 + N_5 + N_{11} + N_{16} + 2N_{17} + N_{30} + 2N_{31} + 3N_{32} + N_{35} + 2N_{36} + 3N_{37} \qquad (14)$$

$-f_4 = -f(CO_3)$

$$N_{04} + N_{08} = N_6 + N_7 + N_8 \qquad (15)$$

$-f_5 = -f(Fe)$

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

$-f_6 = -f(Ce)$

$$N_{01} = N_{26} + N_{27} + 2N_{28} + 2N_{29} + N_{30} + N_{31} + N_{32} + N_{33} + N_{34} + N_{35} + N_{36} + N_{37} \qquad (17)$$

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

$$-N_2 + N_3 + 7N\text{-}_4 + 8N_5 + 4N_6 + 5N_7 + 6N_8 + N_{10} + 8N_{11} + N_{13} + 2N_{14} + 2N_{15} + 8N_{16} + 16N_{17} + N_{27} + 3N_{28} + 4N_{29-} + 8N_{30} + 16N_{31} + 24N_{32} + N_{34} + 8N_{35} + 16N_{36} + 24N_{37} = 16N_{01} + 6N_{02} + 4N_{04} + 8N_{05} + 6N_{06} + 4N_{08} \qquad (18)$$

The linear combination

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

$$(+1)\cdot f(H) + (-2)\cdot f(O) + (+6)\cdot f(SO_4) + (+4)\cdot f(CO_3) - ChB = 0 \qquad (19)$$

involving $K^*=4$ balances for electron-non-active elements: H, O, S, C ($f(SO_4) = f(S)$, $f(CO_3) = f(C)$) gives the equation:

$$2(N_9+N_{10}+N_{11}) + 3(N_{12}+N_{13}+N\text{-}_{14}+2N_{15}+N_{16}+N_{17}) + 4(N_{26}+N_{27}+2N_{28}+2N_{29}+N_{30}+N_{31}+N_{32}) + 3(N_{33}+N_{34}+N_{35}+N_{36}+N_{37}) = 2N_{05} + 4N_{01} \qquad (20)$$

Denoting atomic numbers: $Z_{Fe} = 26$, $Z_{Ce} = 58$, from equations: 16, 17 and 20, we obtain the balance

$Z_{Fe}\cdot f_5 + Z_{Ce}\cdot f_6 - (2\cdot f_2 - f_1 + f_0 - 6f_3 - 4f_4)$

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

Applying the relations:

$$[X_i^{z_i}]\cdot(V_0+V) = 10^3\cdot\frac{N_i}{N_A},\ C_{02}V_0 = 10^3\cdot N_{01}/N_A, \text{ and } CV = 10^3\cdot N_{05}/N_A \qquad (22)$$

in eq. 21, we obtain GEB, written in terms of molar concentrations

$$(Z_{Fe}-2)([Fe^{+2}]+[FeOH^{+1}]+[FeSO_4]) + (Z_{Fe}-3)([Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}] +[FeSO_4^{+1}]+[Fe(SO_4)_2^{-1}]) + (Z_{Ce}-4)([Ce^{+4}]+[CeOH^{+3}]+2[Ce_2(OH)_3^{+5}] +2[Ce_2(OH)_4^{+4}]+[CeSO_4^{+2}] +[Ce(SO_4)_2]+ [Ce(SO_4)_3^{-2}]) + (Z_{Ce}-3)([Ce^{+3}]+[CeOH^{+2}]+[CeSO_4^{+1}] +[Ce(SO_4)_2^{-1}]+[Ce(SO_4)_3^{-3}]) - ((Z_{Fe}-2)\cdot C_{02}V_0 + (Z_{Ce}-4)\cdot CV)/(V_0+V) = 0 \qquad (21a)$$

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

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

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

$$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4] - ([Ce^{+4}]+[CeOH^{+3}]+2[Ce_2(OH)_3^{+5}]+2[Ce_2(OH)_4^{+4}]+ [CeSO_4^{+2}]+[Ce(SO_4)_2]+[Ce(SO_4)_3^{-2}]) - (C_{02}V_0 - CV)/(V_0+V) = 0 \qquad (23a)$$

From eq. 18, considered as the *pr*imary form of Generalized Electron Balance (GEB), f_{12} = *pr*-GEB, we obtain the equation

$$- [H^{+1}] + [OH^{-1}] + 7[HSO_4^{-1}] + 8[SO_4^{-2}] + 4[H_2CO_3] + 5[HCO_3^{-1}] + 6[CO_3^{-2}] + [FeOH^{+1}] + 8[FeSO_4] + [FeOH^{+2}] + 2[Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}]+8[FeSO_4^{+1}]+16[Fe(SO_4)_2^{-1}] + [CeOH^{+3}] + 3[Ce_2(OH)_3^{+5}] +$$

$4[Ce_2(OH)_4^{+4}] + 8[CeSO_4^{+2}] + 16[Ce(SO_4)_2] + 24[Ce(SO_4)_3^{-2}] + [CeOH^{+2}] + 8[CeSO_4^{+1}] +$
$16[Ce(SO_4)_2^{-1}] + 24[Ce(SO_4)_3^{-3}] – (16CV + 6(C_{01}V_0 + C_1V) + 4(C_{02}V_0 + C_2V))/(V_0+V) = 0$ (18a)

where, in addition to relations 22, we apply

$C_1V = 10^3\cdot\frac{N_{02}}{N_A}$, $C_{01}V_0 = 10^3\cdot\frac{N_{06}}{N_A}$, $C_2V = 10^3\cdot\frac{N_{04}}{N_A}$, $C_{02}V_0 = 10^3\cdot\frac{N_{08}}{N_A}$ (24)

From eq. 20 we have

$2\cdot([Fe^{+2}]+[FeOH^{+1}]+[FeSO_4]) + 3\cdot([Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+[FeSO_4^{+1}]+[Fe(SO_4)_2^{-1}]) + 4\cdot([Ce^{+4}]+[CeOH^{+3}]+2[Ce_2(OH)_3^{+5}]+2[Ce_2(OH)_4^{+4}]+[CeSO_4^{+2}] +[Ce(SO_4)_2]+[Ce(SO_4)_3^{-2}]) + 3\cdot([Ce^{+3}]+[CeOH^{+2}] +[CeSO_4^{+1}]+[Ce(SO_4)_2^{-1}]+[Ce(SO_4)_3^{-3}]) – (2\cdot C_0V_0 + 4\cdot CV)/(V_0+V) = 0$ (20a)

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

$[Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+[FeSO_4^{+1}]+[Fe(SO_4)_2^{-1}] –$
$([Ce^{+3}]+[CeOH^{+2}]+[CeSO_4^{+1}]+[Ce(SO_4)_2^{-1}]+[Ce(SO_4)_3^{-3}]) = 0$ (25)

where oxidized forms of Fe and reduced forms of Ce are interrelated; molar concentrations: C_{02} 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:

$[H^{+1}] – [OH^{-1}] – [HSO_4^{-1}] – 2[SO_4^{-2}] – [HCO_3^{-1}] – 2[CO_3^{-2}] + 2[Fe^{+2}] + [FeOH^{+1}] +$
$3[Fe^{+3}] + 2[FeOH^{+2}] + [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}] + [FeSO_4^{+1}] – [Fe(SO_4)_2^{-1}] +$
$4[Ce^{+4}] + 3[CeOH^{+3}] + 5[Ce_2(OH)_3^{+5}] + 4[Ce_2(OH)_4^{+4}] + 2[CeSO_4^{+2}] – 2[Ce(SO_4)_3^{-2}] +$
$3[Ce^{+3}] + 2[CeOH^{+2}] + [CeSO_4^{+1}] – [Ce(SO_4)_2^{--1}] – 3[Ce(SO_4)_3^{-3}] = 0$ (13a)

$[HSO_4^{-1}] + [SO_4^{-2}] + [FeSO_4] + [FeSO_4^{+1}] + 2[Fe(SO_4)_2^{-1}] + [CeSO_4^{+2}] + 2[Ce(SO_4)_2] +$
$3[Ce(SO_4)_3^{-2}] + [CeSO_4^{+1}] + 2[Ce(SO_4)_2^{-1}] + 3[Ce(SO_4)_3^{-3}] –$
$(C_0V_0 + C_{01}V_0 + 2CV + C_1V)/(V_0+V) = 0$ (14a)

$[H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] – (C_{02}V_0 + C_2V)/(V_0+V) = 0$ (15a)

$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4] + [Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+[FeSO_4^{+1}]+[Fe(SO_4)_2^{-1}] – C_{02}V_0/(V_0+V) = 0$ (16a)

$[Ce^{+4}] + [CeOH^{+3}] + 2[Ce_2(OH)_3^{+5}] + 2[Ce_2(OH)_4^{+4}] + [CeSO_4^{+2}] + [Ce(SO_4)_2] + [Ce(SO_4)_3^{-2}] + [Ce^{+3}] + [CeOH^{+2}] + [CeSO_4^{+1}] + [Ce(SO_4)_2^{-1}] + [Ce(SO_4)_3^{-3}] – CV/(V_0+V) = 0$ (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.

$[H^{+1}][OH^{-1}] = 10^{-14.0}$; $[HSO_4^{-1}] = 10^{1.8}[H^{+1}][SO_4^{-2}]$; $[H_2CO_3] = 10^{16.4}[H^{+1}]^2[CO_3^{-2}]$; $[HCO_3^{-1}] = 10^{10.1}[H^{+1}][CO_3^{-2}]$;

$[Fe^{+3}] = [Fe^{+2}]\cdot 10^{A(E – 0.771)}$; $[FeOH^{+1}] =10^{4.5}[Fe^{+2}][OH^{-1}]$; $[FeOH^{+2}] = 10^{11.0}[Fe^{+3}][OH^{-1}]$;

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

$[FeSO_4^{+1}] = 10^{4.18}[Fe^{+3}][SO_4^{-2}]$; $[Fe(SO_4)_2^{-1}] = 10^{7.4}[Fe^{+3}][SO_4^{-2}]^2$;

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

$[MnOH^{+2}] = 10^{14.2}[Mn^{+3}][OH^{-1}]$; $[MnSO_4] = 10^{2.28}\cdot[Mn^{+2}][SO_4^{-2}]$;

$[Ce^{+4}] = [Ce^{+3}]\cdot 10^{A(E–1.70)}$; $[CeOH^{+3}] = 10^{13.3}[Ce^{+4}][OH^{-1}]$; $[Ce_2(OH)_3^{+5}] = 10^{13.3}[Ce^{+4}]^2[OH^{-1}]^3$;

$[Ce_2(OH)_3^{+5}] = 10^{40.3}[Ce^{+4}]^2[OH^{-1}]^3$; $[Ce_2(OH)_4^{+4}] = 10^{53.7}[Ce^{+4}]^2[OH^{-1}]^4$; $[CeOH^{+2}] = 10^{5.0}[Ce^{+3}][OH^{-1}]$; $[CeSO_4^{+1}] = 10^{1.63}[Ce^{+3}][SO_4^{-2}]$; $[Ce(SO_4)_2^{-1}] = 10^{2.34}[Ce^{+3}][SO_4^{-2}]^2$; $[Ce(SO_4)_3^{-3}] = 10^{3.08}[Ce^{+3}][SO_4^{-2}]^3$; $[CeSO_4^{+2}] = 10^{3.5}[Ce^{+4}][SO_4^{-2}]$; $[Ce(SO_4)_2] = 10^{8.0}[Ce^{+4}][SO_4^{-2}]^2$; $[Ce(SO_4)_3^{-2}] = 10^{10.4}[Ce^{+4}][SO_4^{-2}]^3$. (26)

where

$A = 1/\vartheta_0$, $\vartheta_0 = \frac{RT}{F}\cdot\log 10$; $A = 16.9$ at $T = 298$ K. (27)

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(Φ) and/or pH = pH(Φ), with the fraction titrated [25-28]

$$\Phi = \frac{C\cdot V}{C_0\cdot V_0} \qquad (28)$$

on the abscissa, 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 Φ 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

$$\Phi = \frac{C\cdot V}{C_{02}\cdot V_0} \qquad (28a)$$

where $C_0 = C_{02}$.

The fraction titrated Φ (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

$$\Phi_{eq} = \frac{C\cdot V_{eq}}{C_0\cdot V_0} \qquad (29)$$

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(Φ).

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

$$C_0\cdot V_0 = 10^3\cdot\frac{m_A}{M_A} \qquad (30)$$

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

$$m_A = 10^{-3}\cdot C\cdot M_A\cdot\frac{V}{\Phi} \qquad \frac{V}{\Phi} \qquad (31)$$

The value of the fraction in eq. 31, obtained from eq. 28,

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

(32)

is constant during the titration. Particularly, at the end (e) and equivalent (eq) points we have

$$\frac{V}{\Phi} = \frac{V_e}{\Phi_e} = \frac{V_{eq}}{\Phi_{eq}}$$

(33)

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

$$\Phi_e = \frac{C \cdot V_e}{C_0 \cdot V_0}$$

(34)

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

$$m_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_e} \qquad m_A = 10^{-3} \cdot C \cdot V_{eq} \cdot \frac{M_A}{\Phi_{eq}}$$

(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:

$$m'_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_{eq}} \qquad m'_A = 10^{-3} \cdot C \cdot V_e \cdot R_A^{eq}$$

□ (36)

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

$$R_A^{eq} = \frac{M_A}{\Phi_{eq}}$$

(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.

```
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

pH=x(1);
E=x(2);
Mn2=10.^-x(3);
Fe2=10.^-x(4);
SO4=10.^-x(5);
H2CO3=10.^-x(6);

H=10.^-pH;
pKw=14;
Kw=10.^-14;
OH=Kw./H;
A=16.9;
ZFe=26;
ZMn=25;

Mn7O4=Mn2.*10.^(5.*A.*(E-1.507)+8.*pH);
Mn6O4=Mn2.*10.^(4.*A.*(E-1.743)+8.*pH);
Mn3=Mn2.*10.^(A.*(E-1.509));

Fe3=Fe2.*10.^(A.*(E-0.771));

HSO4=10.^1.8.*H.*SO4;
HCO3=10.^(pH-6.3)*H2CO3.
CO3=10^(pH-10.1)*HCO3.

Fe2OH=10.^4.5.*Fe2.*OH;
Fe2SO4=10.^2.3.*Fe2.*SO4;

Fe3OH=10.^11.0.*Fe3.*OH;
```

```
Fe3OH2=10.^21.7.*Fe3.*OH.^2;
Fe32OH2=10.^25.1.*Fe3.^2.*OH.^2;
Fe3SO4=10.^4.18.*Fe3.*SO4;
Fe3SO42=10.^7.4.*Fe3.*SO4.^2;
Mn2OH=10.^3.4.*Mn2.*OH;
Mn2SO4=10.^2.28.*Mn2.*SO4;
Mn3OH=10.^14.2.*Mn3.*OH;
K=C.*V./(V0+V);

   %Charge balance
F=[(H-OH+K-HSO4-HCO3-2.*CO3-2.*SO4-Mn7O4-2.*Mn6O4...
   +3*Mn3+2.*Mn3OH+2.*Mn2+Mn2OH+2.*Fe2+Fe2OH+3.*Fe3...
   +2.*Fe3OH+Fe3OH2+4.*Fe32OH2+Fe3SO4-Fe3SO42);

   %Concentration balance of Mn
  (Mn7O4+Mn6O4+Mn3+Mn3OH+Mn2+Mn2OH+Mn2SO4-C.*V./(V0+V));

   %Concentration balance of Fe
  (Fe2+Fe2OH+Fe2SO4+Fe3+Fe3OH+Fe3OH2+2.*Fe32OH2...
  +Fe3SO4+Fe3SO42-C02.*V0./(V0+V));

   %Concentration balance of S
   (HSO4+SO4+Mn2SO4+Fe2SO4+Fe3SO4+2.*Fe3SO42...
   -(C02+C04).*V0./(V0+V));

   %Concentration balance of C
   (H2CO3+HCO3+CO3-(C2*V+C05*V0)./(V0+V);

   %Electron balance
   ((ZMn-7).*Mn7O4+(ZMn-6).*Mn6O4+(ZMn-3).*(Mn3+Mn3OH)...
   +(ZMn-2).*(Mn2+Mn2OH+Mn2SO4)+(ZFe-2).*(Fe2+Fe2OH+Fe2SO4)...
   +(ZFe-3).*(Fe3+Fe3OH+Fe3OH2+Fe32OH2+Fe3SO4+Fe3SO42)...
   -((ZFe-2).*C02.*V0+(ZMn-7).*C.*V)./(V0+V))];

logMn2=log10(Mn2);
logMn2OH=log10(Mn2OH);
logMn2SO4=log10(Mn2SO4);
logMn3=log10(Mn3);
logMn3OH=log10(Mn3OH);
logMn6O4=log10(Mn6O4);
```

```
logMn7O4=log10(Mn7O4);
logFe2=log10(Fe2);
logFe2OH=log10(Fe2OH);
logFe2SO4=log10(Fe2SO4);
logFe3=log10(Fe3);
logFe3OH=log10(Fe3OH);
logFe3OH2=log10(Fe3OH2);
logFe32OH2=log10(Fe32OH2);
logFe3SO4=log10(Fe3SO4);
logFe3SO42=log10(Fe3SO42);
logHSO4=log10(HSO4);
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 $\Phi = \Phi_{eq} = 0.2$, named as equivalent (eq) point; note that $0.20000 \equiv \frac{1}{5} \equiv 1 : 5$. The coordinates of equivalent point are $(\Phi_{eq}, E_{eq}) = (0.20000, 1.034)$, with Φ_{eq} as the stoichiometric point of the reaction

$$MnO_4^{-1} + 5Fe^{+2} + 8H^{+1} = Mn^{+2} + 5Fe^{+3} + 4H_2O \qquad (39)$$

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

$$MnO_4^{-1} + 5FeSO_4 + 6HSO_4^{-1} + 2H^{+1} = MnSO_4 + 5Fe(SO_4)_2^{-1} + 4H_2O \qquad (40)$$

No changes in slope on the pH = pH(Φ) curves occur at $\Phi_{eq} = 0.2$ (Fig. 1b), although one would expect, at first glance, that MnO_4^{-1} may act, especially in reaction 39, like 'octopus' swallowing H^{+1} at $\Phi < 0.2$, while the reaction 39 does not occur at $\Phi > 0.2$. 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).

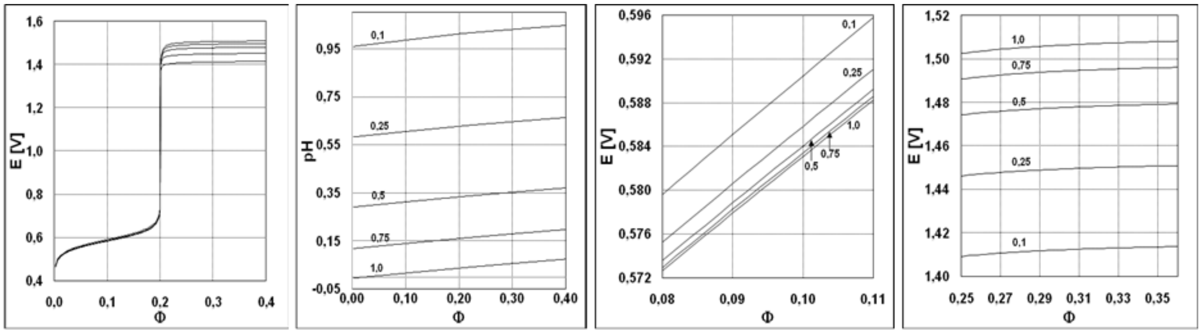

Fig. 1. The (1a) E = E(Φ) and (1b) pH = pH(Φ) curves plotted for the System I at $V_0 = 100$, $(C_{02-},V_0,C) = (0.01,100, 0.02)$ and different C_{04} values [mol/L], indicated in Figures 1b, 1c and 1d (in enlarged scales), before and after $\Phi_{eq} = 0.2$; $C_2=C_{05}=0$.

Table 1. The pairs of (Φ, 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 (Φ_{eq}, E_{eq}); E in NHE scale.

Φ	E [V]
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

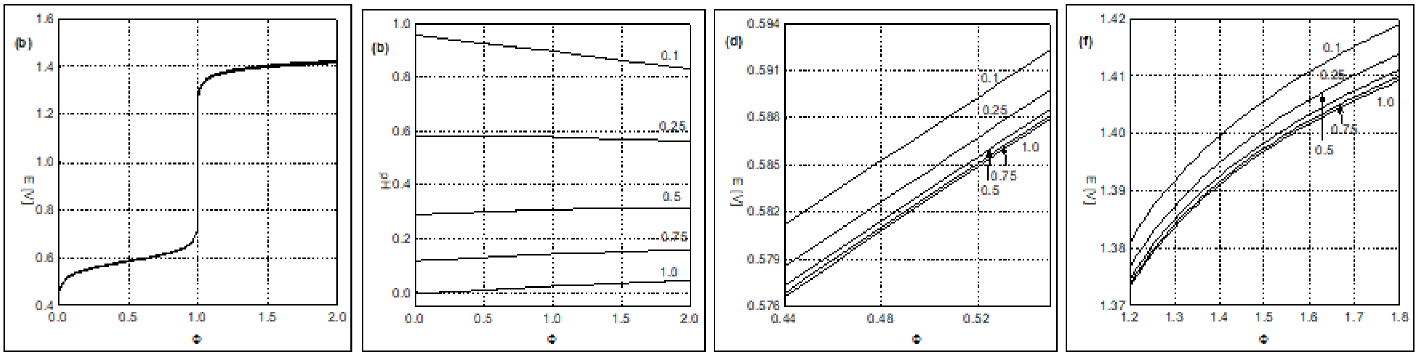

Fig. 2. The (2a) E = E(Φ) and (2b) pH = pH(Φ) curves plotted for the System III at V_0 = 100, (C_{02-},V_0,C,C_1) = (0.01,100, 0.1,1.0) and different C_{04} values [mol/L], indicated in Figures 2b, 2c and 2d (in enlarged scales), before and after Φ_{eq} = 1.0; C_2=C_{05}=0.

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

$$Fe^{+3} + e^{-1} = Fe^{+2} \qquad (41)$$

is expressed by the Nernst equation

$$E = E_0^* + \vartheta \cdot \log\frac{[Fe^{+3}]}{[Fe^{+2}]} = E_0^* + a \cdot \ln\frac{[Fe^{+3}]}{[Fe^{+2}]} \qquad (42)$$

where ϑ = a·ln10 is the real slope of indicator electrode; ϑ 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.

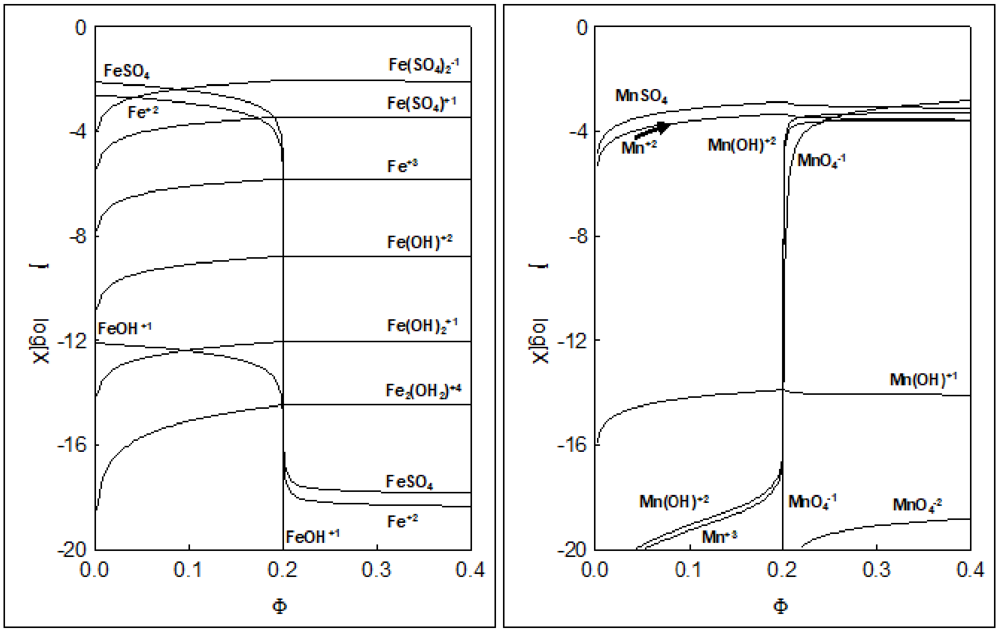

Fig. 3. Dynamic speciation diagrams for (3a) Fe-species, (3b) Mn-species in the System I ; (C_{02},C,C_{04}) = (0.01,0.02,1.0), $C_2=C_{05}=0$, $V_0=100$.

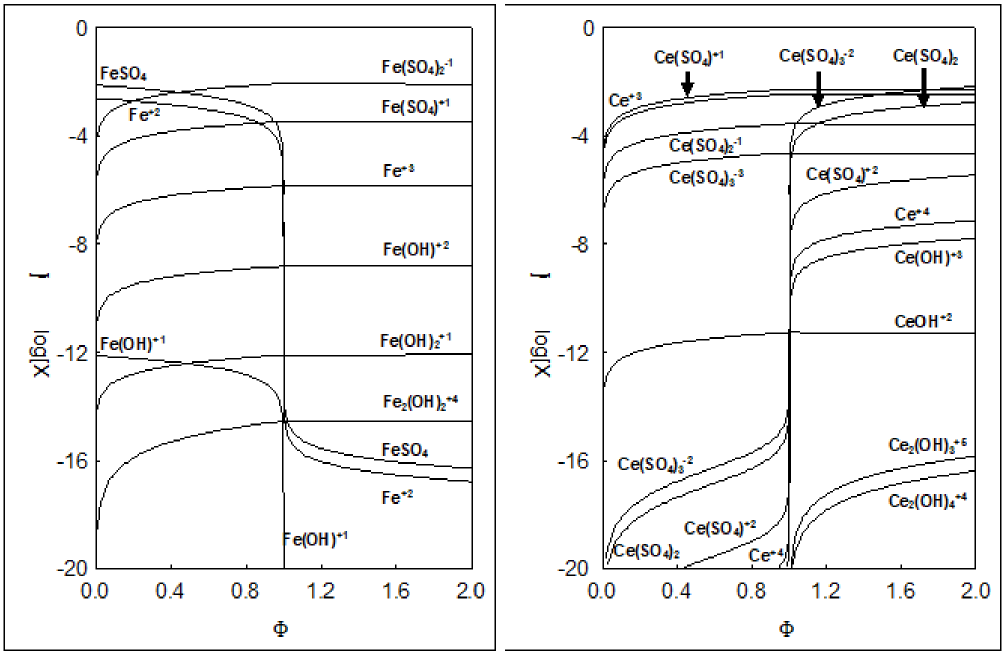

Fig.4. Dynamic speciation diagrams for (4a) Fe-species, (4b) Ce-species in the System III; (C,C_1,C_{02},C_{04}) = (0.1,0.5,0.02,1.0), $C_2=C_{05}=0$, $V_0=100$.

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_2SO_4 (C_{04}) as D. The GEB expressed by eq. 11a, and rewritten as follows:

$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4] – (5[MnO_4^{-1}]+4[MnO_4^{-2}]+[Mn^{+3}]+[MnOH^{+2}])$
$= (C_{02}V_0 – 5CV)/(V_0+V)$ (11b)

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

$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4] + [Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+[FeSO_4^{+1}]+[Fe(SO_4)_2^{-1}]$
$= (C_{02}+2C_{03})V_0/(V_0+V)$ (4b)

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

$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4]+[Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}].+[FeSO_4^{+1}]+[Fe(SO_4)_2^{-1}]$
$= C_{02}V_0/(V_0+V)$ (4c)

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

$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4] – ([Ce^{+4}]+[CeOH^{+3}]+2[Ce_2(OH)_3^{+5}]+2[Ce_2(OH)_4^{+4}]+$
$[CeSO_4^{+2}]+[Ce(SO_4)_2]+[Ce(SO_4)_3^{-2}]) = (C_{02}V_0 – CV)/(V_0+V)$, and (23b)
$[Fe^{+2}]+[FeOH^{+1}]+[FeSO_4] + [Fe^{+3}]+[FeOH^{+2}]+[Fe(OH)_2^{+1}]+2[Fe_2(OH)_2^{+4}]+[FeSO_4^{+1}]+[Fe(SO_4)_2^{-1}]$
$= C_{02}V_0/(V_0+V)$ (16b)

The latter one is identical with eq. 4c.

9.2. Derivation of formulas for the Systems I and III

From relations: $CV = \underline{\Phi}\cdot C_{02}V_0$, and $CV_{eq} = \Phi_{eq}\cdot C_{02}V_0$, we have

$$\frac{V}{V_{eq}} = \frac{\Phi}{\Phi_{eq}} \quad (43)$$

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:

$[Fe^{+2}] + [FeSO_4] = (C_{02}V_0 – 5CV)/(V_0+V)$ (at $\Phi_{eq} < 0.2$, for the Systems I, II) (11c)
$[Fe^{+2}] + [FeSO_4] = (C_{02}V_0 – CV)/(V_0+V)$ (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

$[Fe^{+2}] + [FeSO_4] + [Fe^{+3}] + [FeSO_4^{+1}] + [Fe(SO_4)_2^{-1}] = C_{02}V_0/(V_0+V)$ (4c)

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

$[Fe^{+2}]\cdot b_2 = (C_{02}V_0 – 5CV)/(V_0+V)$ (11d)
$[Fe^{+2}]\cdot b_2 = (C_{02}V_0 – CV)/(V_0+V)$ (23d)
$[Fe^{+2}]\cdot b_2 + [Fe^{+3}]\cdot b_3 = C_{02}V_0/(V_0+V)$ (4d)

where : $b_2 = 1 + 10^{2.3}\times[SO_4^{-2}]$, $b_3 = 1 + 10^{4.18}\times[SO_4^{-2}] + 10^{7.4}\times[SO_4^{-2}]^2$, i.e.,

$$\frac{b_3}{b_2} = \frac{1+10^{4.18}\cdot[SO_4^{-2}]+10^{7.4}\cdot[SO_4^{-2}]^2}{1+10^{2.3}\cdot[SO_4^{-2}]} \quad (44)$$

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

$$1 + \frac{b_3}{b_2}\cdot\frac{[Fe^{+3}]}{[Fe^{+2}]} = \frac{1}{1-5\cdot\Phi} \quad \square \quad \frac{[Fe^{+3}]}{[Fe^{+2}]} = \frac{b_2}{b_3}\cdot\frac{5\cdot\Phi}{1-5\cdot\Phi} = \frac{b_2}{b_3}\cdot\frac{V}{V_{eq}-V} \quad (45)$$

whereas from equations: 23d, 4d, 43 and $\Phi_{eq} = 1$, we have

$$1 + \frac{b_3}{b_2} \cdot \frac{[Fe^{+3}]}{[Fe^{+2}]} = \frac{1}{1-\Phi} \quad \Rightarrow \quad \frac{[Fe^{+3}]}{[Fe^{+2}]} = \frac{b_2}{b_3} \cdot \frac{\Phi}{1-\Phi} \quad = \frac{b_2}{b_3} \cdot \frac{V}{V_{eq}-V} \qquad (46)$$

i.e., the expressions for the ratio $\frac{[Fe^{+3}]}{[Fe^{+2}]}$ are identical in the Systems: I and III. In the System III, the value of $\frac{b_3}{b_2}$ (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

$$E = E_0^* - a \cdot \ln\frac{b_3}{b_2} + a \cdot \ln V - a \cdot \ln(V_{eq} - V) \qquad (47)$$

valid for $V < V_{eq}$.

The $\theta = \ln\frac{b_3}{b_2}$ vs. Φ relationships [10] are plotted for the Systems: I (Fig. 5a) and III (Fig. 5b). We see that $\frac{d\theta}{d\Phi} < 0$ in Fig. 5a, and $\frac{d\theta}{d\Phi} < 0$ in Fig. 5b. The θ vs. Φ relationships are *quasi*-linear, especially for greater C_{04} values. Then we can assume the relation

$$\ln\frac{b_3}{b_2} = \alpha - \gamma \cdot \Phi = \alpha - \beta \cdot V \qquad (48)$$

where a, g and b = $\frac{\gamma \cdot C}{C_0 \cdot V_0}$ denote constant values for the given titration. Applying eq. 48 in eq. 47, we have

$$E = \omega + a \cdot \beta \cdot V + a \cdot \ln V - a \cdot \ln(V_{eq} - V) \qquad (49)$$

where ω = $E_0^* - a \cdot \alpha$ is the new constant value, obtained from constant values introduced above. From eq. 49 we have, by turns,

$$\frac{E-\omega}{a} = \beta \cdot V + \ln\frac{V}{V_{eq}-V} \quad \Rightarrow \quad \frac{E-\omega}{\vartheta} = \frac{\beta}{\ln 10} \cdot V + \log\frac{V}{V_{eq}-V} \quad \Rightarrow$$

$$\Omega = e^{-\frac{\omega}{a}} \cdot e^{-\beta \cdot V} \cdot (V_{eq} - V) \qquad (50)$$

where $\vartheta = a \cdot \ln 10$, and

$$\Omega = V \cdot 10^{-\frac{E}{\vartheta}} \qquad (51)$$

At high C_{04} value, the change of $\theta = \ln\frac{b_3}{b_2}$ value is relatively small (Figures 5a,b); b = 1.7×10^{-3} at C_{04} = 1 mol/L. Then the assumption $\ln\frac{b_3}{b_2}$ = const can be applied below in the simplified model. Putting β = 0 in eq. 50, we get

$$\Omega = G_2 \cdot (V_{eq} - V) \qquad (52)$$

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

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

$$\Omega = P \cdot V^2 - Q \cdot V + R \qquad (53)$$

where:

$$P = G_2 \cdot \beta \text{ , } Q = G_2 \cdot (\beta \cdot V_{eq} + 1) \text{ , } R = G_2 \cdot V_{eq} \qquad (54)$$

Eq. 53 rewritten in the form of regression equation

$$\Omega_j = V_j \cdot 10^{-\frac{E_j}{\vartheta}} = P \cdot V_j^2 - Q \cdot V_j + R + \varepsilon_j \qquad (53a)$$

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,

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

$$V_{eq} = \frac{Q - \sqrt{Q^2 - 4 \cdot P \cdot R}}{2 \cdot P} \qquad (55)$$

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 ϑ value for the slope of an indicator electrode.

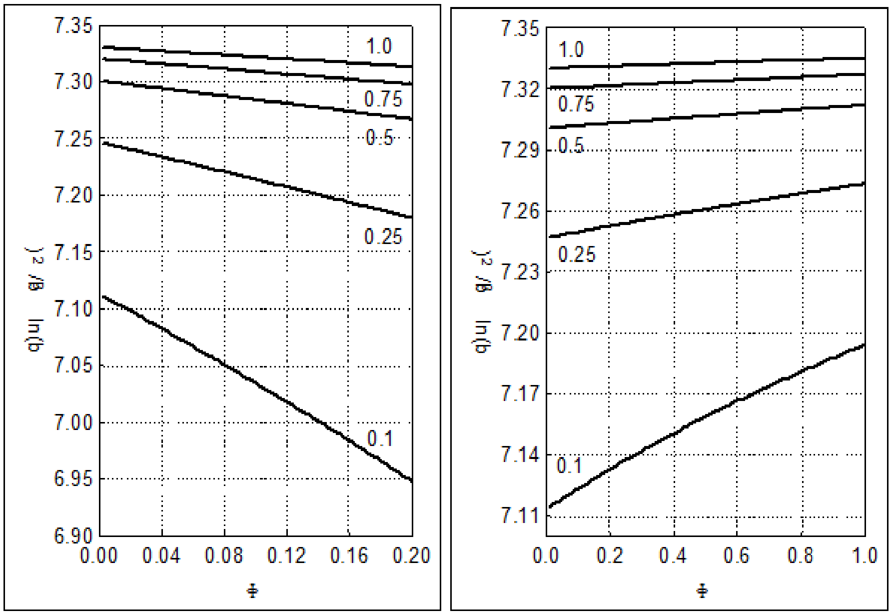

Fig. 5. The q = ln(b_3/b_2) vs. F relationships for the Systems: I (5a), at (C,C_{02}) = (0.02,0.01), and III (5b), plotted at (C,C_1,C_{02}) = (0.1,0.5,0.01), V_0=100, C_2=C_{05}=0, and different C_{04} values indicated at the corresponding curves.

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

$$E_{j+1} - E_j = a \cdot \beta \cdot \left(V_{j+1} - V_j\right) + a \cdot \ln\frac{V_{j+1}}{V_j} - a \cdot \ln\frac{V_{eq} - V_{j+1}}{V_{eq} - V_j} \qquad (56)$$

Applying in eq. 56 the identities:

$$\frac{V_{j+1}}{V_j} = 1 + x_{1j} \text{ , } \frac{V_{eq} - V_{j+1}}{V_{eq} - V_j} = 1 - x_{2j}$$

where :

$$x_{1j} = \frac{V_{j+1}-V_j}{V_j} \quad , \quad x_{2j} = \frac{V_{j+1}-V_j}{V_{eq}-V_j} \qquad (57)$$

we get

$$E_{j+1} - E_j = a \cdot \beta \cdot (V_{j+1} - V_j) + a \cdot \ln(1 + x_{1j}) - a \cdot \ln(1 - x_{2j}) \qquad (58)$$

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

$$\ln(1 + x_{1j}) \cong \left(\frac{1}{x_{1j}} + \frac{1}{2}\right)^{-1} \quad \Leftrightarrow \quad \ln(1 - x_{1j}) \cong \left(\frac{1}{x_{1j}} - \frac{1}{2}\right)^{-1} \qquad (59)$$

we write

$$\ln(1 + x_{1j}) - \ln(1 - x_{2j}) = \left(\frac{1}{x_{1j}} + \frac{1}{2}\right)^{-1} + \left(\frac{1}{x_{2j}} - \frac{1}{2}\right)^{-1} \qquad (60a)$$

$$= 4 \cdot \frac{x_{1j}+x_{2j}}{(2+x_{1j})(2-x_{2j})} = \frac{(V_{j+1}-V_j)\cdot V_{eq}}{V_j^*\cdot(V_{eq}-V_j^*)} = (V_{j+1} - V_j) \cdot \left(\frac{1}{V_j^*} + \frac{1}{V_{eq}-V_j^*}\right) \qquad (60b)$$

where

$$V_j^* = \frac{V_j+V_{j+1}}{2} \qquad (61)$$

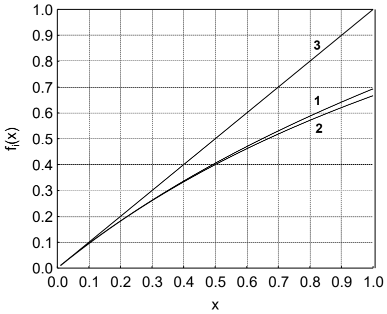

Fig. 6. Comparison of the plots for: (1) $f_1(x) = \ln(1+x)$, (2) $f_2(x) = \left(\frac{1}{x} + \frac{1}{2}\right)^{-1}$ and (3) $f_3(x) = x$, x □ < 0, 1 > .

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

$$y_j^* = \frac{E_{j+1}-E_j}{V_{j+1}-V_j} = a \cdot \beta + a \cdot \left(\frac{1}{V_j^*} + \frac{1}{V_{eq}-V_j^*}\right) \qquad (62)$$

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

$$SS = \sum_j \left(a \cdot \beta + a \cdot \left(\frac{1}{V_j^*} + \frac{1}{V_{eq}-V_j^*}\right) - y_j^*\right)^2 \qquad (63)$$

9.4. Approximate models (β=0)

***Model 1**.*

Putting β = 0 in eq. 62, we get, after transformation

$$y_j^* = \frac{1}{V_j^*} \cdot \frac{V_{j+1}-V_j}{E_{j+1}-E_j} = G_I \cdot (V_{eq} - V_j^*) \qquad (64)$$

where

$$G_I = \frac{1}{a \cdot V_{eq}} \qquad (65)$$

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

$$R = G_I \cdot V_{eq} \qquad (66)$$

from eq. 58 we have the regression equation

$$y_j^* = R - G_I \cdot V_j^* + \varepsilon_j \qquad (67)$$

The R and G_I are determined there according to LSM:

$$R = \frac{\Sigma y_j^* \cdot \Sigma V_j^{*2} - \Sigma V_j^* \cdot \Sigma y_j^* V_j^*}{(N-1) \cdot \Sigma V_j^{*2} - (\Sigma V_j^*)^2} \quad ; \quad G_I = -\frac{(N-1) \cdot \Sigma y_j^* V_j^* - \Sigma y_j^* \cdot \Sigma V_j^*}{(N-1) \cdot \Sigma V_j^{*2} - (\Sigma V_j^*)^2} \qquad (68)$$

and then we get

$$V_{eq} = \frac{R}{G_I} = \frac{\Sigma V_j^* \cdot \Sigma y_j^* V_j^* - \Sigma y_j^* \cdot \Sigma V_j^{*2}}{(N-1) \cdot \Sigma y_j^* V_j^* - \Sigma y_j^* \cdot \Sigma V_j^*} \qquad (69)$$

where $\Sigma = \Sigma_{j=1}^{N-1}$ in equations 68, 69; N – number of exp. points $(V_j,E_j) \mid j=1,\ldots,N$. The formulation applied here is the basis for the modified G(I) method in its simplified version, denoted as MG(I)S version [10]. The great advantage of MG(I)S over G(I) method results from application of formulas 59 instead of approximation ln(1±x) ≈ ± 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 Ω (eq. 51) [11]:

$$\frac{d\Omega}{dV} = 10^{-\frac{E}{\vartheta}} \cdot \left(1 - \frac{\ln 10}{\vartheta} \cdot V \cdot \frac{dE}{dV}\right) \qquad (70)$$

$$\frac{d^2\Omega}{dV^2} = 10^{-\frac{E}{\vartheta}} \cdot \frac{\ln 10}{\vartheta} \cdot \left(V \cdot \frac{d^2E}{dV^2} + 2 \cdot \frac{dE}{dV} - \frac{\ln 10}{\vartheta} \cdot V \cdot \left(\frac{dE}{dV}\right)^2\right) \qquad (71)$$

Note that the first derivative of eq. 52 is $\frac{d\Omega}{dV} =$ – G_2 = const (at β=0); then $\frac{d^2\Omega}{dV^2} = 0$. Zeroing the second derivative (eq. 71) gives

$$\vartheta = \ln 10 \cdot \frac{V \cdot \left(\frac{dE}{dV}\right)^2}{V \cdot \frac{d^2E}{dV^2} + 2 \cdot \frac{dE}{dV}} \qquad (72)$$

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

$$\vartheta \cong \ln 10 \cdot \frac{V \cdot \left(\frac{\Delta E}{\Delta V}\right)^2}{V \cdot \frac{\Delta^2 E}{\Delta V^2} + 2 \cdot \frac{\Delta E}{\Delta V}} \qquad (72a)$$

where

$$\frac{\Delta^2 E}{\Delta V^2} = \frac{\Delta\left(\frac{\Delta E}{\Delta V}\right)}{\Delta V}$$

For the set of experimental points $\{(V_j, E_j) \mid j = 1,\ldots, N-1\}$, 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 $\frac{\Delta^2 E}{\Delta V^2}$ are put at V_j^* (eq. 61). Then the $J_j = J(V_j)$ 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

$$[Fe^{+2}]\cdot b_2 + [Fe^{+3}]\cdot b_3 = (C_{02}+C_{03})\cdot \frac{V_0}{V_0+V} \qquad (73)$$

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

$$1+\frac{[Fe^{+3}]}{[Fe^{+2}]}\cdot\frac{b_3}{b_2} = \frac{(C_{02}+C_{03})V_0}{C_{02}V_0-5CV}$$

$$\frac{[Fe^{+3}]}{[Fe^{+2}]}\cdot\frac{b_3}{b_2} = \frac{C_{03}V_0+5CV}{C_{02}V_0-5CV} = \frac{\frac{C_{03}}{C_{02}}\cdot C_{02}V_0+5CV}{C_{02}V_0-5CV} = \frac{\frac{C_{03}}{C_{02}}+\frac{5CV}{C_{02}V_0}}{1-\frac{5CV}{C_{02}V_0}} = \frac{\frac{C_{03}}{C_{02}}+\frac{V}{V_{eq}}}{1-\frac{V}{V_{eq}}} = \frac{\frac{C_{03}}{C_{02}}V_{eq}+V}{V_{eq}-V} \qquad (74)$$

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

$$E = E_0^* - a\cdot\ln\frac{b_3}{b_2} + a\cdot\ln\left(\frac{C_{03}}{C_{02}}\cdot V_{eq}+V\right) - a\cdot\ln(V_{eq}-V) \qquad (75)$$

Assuming $\ln\frac{b_3}{b_2}$ = 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

$$E_{j+1}-E_j = a\cdot\ln\left(\frac{\frac{C_{03}}{C_{02}}\cdot V_{eq}+V_{j+1}}{\frac{C_{03}}{C_{02}}\cdot V_{eq}+V_j}\right) - a\cdot\ln\left(\frac{V_{eq}-V_{j+1}}{V_{eq}-V_j}\right) \qquad (76)$$

Denoting

$$x_{1j} = \frac{V_{j+1}-V_j}{\frac{C_{03}}{C_{02}}\cdot V_{eq}+V_j} \quad ; \quad x_{2j} = \frac{V_{j+1}-V_j}{V_{eq}-V_j} \qquad (77)$$

from eq. 76 we get

$$E_{j+1}-E_j = a\cdot\ln(1+x_{1j}) - a\cdot\ln(1-x_{2j}) \qquad (78)$$

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

$$E_{j+1}-E_j = a\cdot\frac{1}{\frac{1}{2}+\frac{\frac{C_{03}}{C_{02}}\cdot V_{eq}+V_j}{V_{j+1}-V_j}} - a\cdot\frac{1}{\frac{1}{2}-\frac{V_{eq}-V_j}{V_{j+1}-V_j}}$$

$$\frac{E_{j+1}-E_j}{V_{j+1}-V_j} = a\cdot\left(\frac{1}{V_j^*+\frac{C_{03}}{C_{02}}\cdot V_{eq}} + \frac{1}{V_{eq}-V_j^*}\right)$$

$$\frac{E_{j+1}-E_j}{V_{j+1}-V_j} = a\cdot\left(\frac{V_{eq}(C_{02}+C_{03})}{(C_{02}\cdot V_j^*+C_{03}\cdot V_{eq})(V_{eq}-V_j^*)}\right)$$

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

$$u_j = P + Q\cdot V_j^* - R\cdot {V_j^*}^2 + \varepsilon_j \qquad (79)$$

where $\Phi_{eq} = \frac{1}{5}$,

$$P = \frac{C_{02} \cdot C_{03} \cdot V_0}{5 \cdot a \cdot C \cdot (C_{02}+C_{03})} \; ; \quad Q = \frac{C_{02}-C_{03}}{a \cdot (C_{02}+C_{03})} \; ; \quad R = \frac{5 \cdot C}{a \cdot (C_{02}+C_{03}) \cdot V_0} \qquad (80)$$

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 assumed. Then we calculate [9]

$$\frac{P}{R} = \left(\frac{V_0}{5C}\right)^2 \cdot C_{02} \cdot C_{03} \; ; \quad \frac{Q}{R} = \frac{V_0}{5C} \cdot (C_{02} - C_{03}) \qquad (81)$$

$$\text{(a)} \quad C_{02} = \frac{5 \cdot C}{2 \cdot V_0} \cdot \left[\sqrt{\left(\frac{Q}{R}\right)^2 + 4 \cdot \frac{P}{R}} + \frac{Q}{R}\right] \; ;\text{(b)} \quad C_{03} = \frac{5 \cdot C}{2 \cdot V_0} \cdot \left[\sqrt{\left(\frac{Q}{R}\right)^2 + 4 \cdot \frac{P}{R}} - \frac{Q}{R}\right] \qquad (82)$$

One should note that the factor $a = \frac{\vartheta}{\ln 10}$ 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,..., 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 [9] are applicable here:

$$\sum_{j=1}^{N} (2j-1) = N^2 \; ; \quad \sum_{j=1}^{N} (2j-1)^2 = \frac{1}{3} \cdot N(4N^2-1) \; ; \quad \sum_{j=1}^{N} (2j-1)^3 = N^2(2N^2-1) \; ;$$

$$\sum_{j=1}^{N} (2j-1)^4 = \frac{1}{15} \cdot N(4N^2-1)(12N^2-7)$$

Then we have:

$$\frac{P}{R} = \left(\frac{\Delta V}{2}\right)^2 \cdot \frac{\begin{vmatrix} \sum_{j=1}^{N-1} u_j & \sum_{j=1}^{N-1}(2j+1) & \sum_{j=1}^{N-1}(2j+1)^2 \\ \sum_{j=1}^{N-1}(2j+1) \cdot u_j & \sum_{j=1}^{N-1}(2j+1)^2 & \sum_{j=1}^{N-1}(2j+1)^3 \\ \sum_{j=1}^{N-1}(2j+1)^2 \cdot u_j & \sum_{j=1}^{N-1}(2j+1)^3 & \sum_{j=1}^{N-1}(2j+1)^4 \end{vmatrix}}{\begin{vmatrix} \sum_{j=1}^{N-1} u_j & \sum_{j=1}^{N-1}(2j+1) & N-1 \\ \sum_{j=1}^{N-1}(2j+1) \cdot u_j & \sum_{j=1}^{N-1}(2j+1)^2 & \sum_{j=1}^{N-1}(2j+1) \\ \sum_{j=1}^{N-1}(2j+1)^2 \cdot u_j & \sum_{j=1}^{N-1}(2j+1)^3 & \sum_{j=1}^{N-1}(2j+1)^2 \end{vmatrix}}$$

$$\frac{Q}{R} = \frac{\Delta V}{2} \cdot \frac{\begin{vmatrix} \sum_{j=1}^{N-1} u_j & N-1 & \sum_{j=1}^{N-1}(2j+1)^2 \\ \sum_{j=1}^{N-1}(2j+1) \cdot u_j & \sum_{j=1}^{N-1}(2j+1) & \sum_{j=1}^{N-1}(2j+1)^3 \\ \sum_{j=1}^{N-1}(2j+1)^2 \cdot u_j & \sum_{j=1}^{N-1}(2j+1)^2 & \sum_{j=1}^{N-1}(2j+1)^4 \end{vmatrix}}{\begin{vmatrix} \sum_{j=1}^{N-1} u_j & \sum_{j=1}^{N-1}(2j+1) & N-1 \\ \sum_{j=1}^{N-1}(2j+1) \cdot u_j & \sum_{j=1}^{N-1}(2j+1)^2 & \sum_{j=1}^{N-1}(2j+1) \\ \sum_{j=1}^{N-1}(2j+1)^2 \cdot u_j & \sum_{j=1}^{N-1}(2j+1)^3 & \sum_{j=1}^{N-1}(2j+1)^2 \end{vmatrix}}$$

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_c) slope values, $|J_c - J|$ for RIEs has been proved [10]. It was also stated that the error in V_{eq} can be substantially decreased, even at greater $|J_c - J|$ 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 ϑ-value of an indicator electrode.

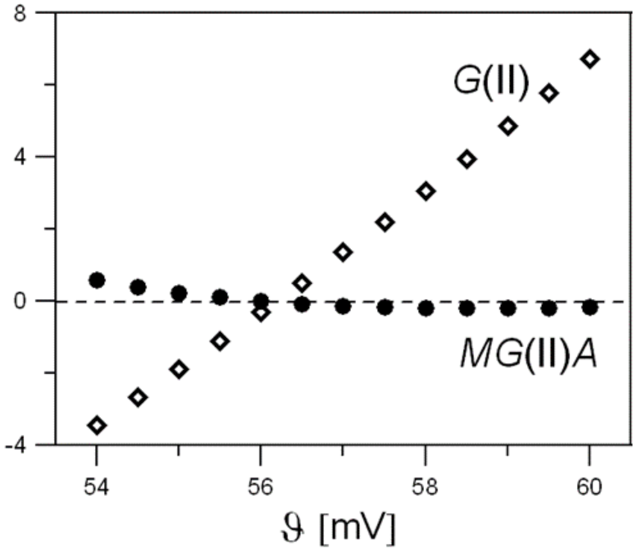

Fig. 7. The relationships between relative error e [%] in V_{eq} determination vs J [mV] plotted for G(II) and MG (II)A methods, at J_c = 56 mV value pre-assumed in calculations [11].

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_{eq}; 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 ϑ – provided that ϑ is constant within defined V-range covered in the Gran methods, where the validity of assumption $\vartheta = \vartheta(V) = const$ 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.

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