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Formulation of Dynamic Redox Systems according to GATES/GEB Principles

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Two equivalent approaches to formulation of generalized electron balance (GEB) concept, needed for resolution of electrolytic redox systems according to GATES/GEB principles, are presented in two examples of simulated potentiometric titrations made with $KMnO_4$ solution as titrant. The results obtained from calculations made according to MATLAB iterative computer programs are presented graphically and discussed. The problems of completeness and consistency of physicochemical knowledge related to the system considered and the resulting consequences, are also discussed.

Keywords: Electrolytic redox systems; titration; generalized electron balance.

1. INTRODUCTION

In aqueous solutions of electrolytes, different components $X_i^{z_i}$ exist as hydrated species, $X_i^{z_i} \cdot n_i H_2O$; $n_i \geq 0$ is the mean number of water molecules attached to $X_i^{z_i}$, z_i is a charge of this species, expressed in terms of elementary charge units, $e = F/N_A$ (F = Faraday constant, N_A = Avogadro number). For these species we apply the notation [1-7]

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

where N_i is a number of these entities (individual species) in a defined system. On this basis, the numbers of particular elements in these species are calculated; e.g., in Example 1, N_{14} entities $MnSO_4 \cdot n_{14}H_2O$ contain $N_{14} \cdot 2n_{14}$ atoms of H, $N_{14}(4+n_{14})$ atoms of O, N_{14} atoms of Mn, and N_{14} atoms of S. The term "core", considered as a cluster/group of elements of defined composition (expressed by chemical formula), structure and charge, is alternatively introduced; e.g., SO_4^{2-} ion is a common core in $HSO_4^- \cdot n_5H_2O$, $SO_4^{2-} \cdot n_6H_2O$, and $MnSO_4 \cdot n_{14}H_2O$ in Example 1. The elements or/and cores in the system in question are involved in the related elemental or/and core balances, supplemented by charge balance

$$\sum_{i=1}^{p} z_i \cdot N_i = 0 \qquad (2)$$

expressing the principle of electroneutrality of the solution; p is a number of kinds of different charged ($z_i \neq 0$) components of i-th kind $X_i^{z_i}$ in this system (i = 1,…,p); for uncharged (z_j=0) components $X_j^{z_j}$ we have $z_j \cdot N_j = 0 \cdot N_j = 0$ for j ≠ i.

The basic component of any aqueous electrolytic system is water, where two elements: $E(1)$ = H and $E(2)$ = O are involved. Other elements $E(k)$ (k ≥ 2) are also involved in such a system, as a rule (k = 1,2,…,K); K = 2, e.g. for aqueous solution of H_2O_2.

Any electrolytic system with aqueous solution can be composed from water and one or more (solid, liquid and/or gaseous) solutes introduced in it. The resulting mixture can be monophase (solution) or polyphase system. The electrolytic system thus obtained is limited to condensed (liquid or liquid+solid) phases.

It is assumed that the system thus formed is the closed system that does not exchange the matter with its environment; an exchange of energy is possible, however. This way, a specified (exothermic or endothermic) process in a system can be carried out under isothermal conditions. In the thermodynamic description of electrolytic systems, the isothermal course of processes is important, because the temperature is one of the main factors securing stability of the equilibrium constant values; another factor is an ionic strength (I, mol/L) of the solution. Any dynamic (e.g., titration) process occurs in a *quasistatic* manner, under isothermal conditions.

The charge (Eq. 2) and elemental/core balances are formulated for closed systems. An elemental balance for $E(k)$ expresses the relationship between the number of atoms of $E(k)$ in components forming the systems and the number of atoms of $E(k)$ in the species in the system thus formed. The elemental balance for $E(k)$ will be denoted by $f(E(k))$. In particular, we have the balances $f(H)$ for H and $f(O)$ for O.

In redox systems, the fundamental role plays the balance $2\cdot f(O) - f(H)$, considered as the *pr*imary form of the generalized electron balance (GEB) [1-14], *pr*-GEB = $2\cdot f(O) - f(H)$. For any redox systems, the *pr*-GEB is linearly independent on charge balance and elemental balances $f(E(k))$ for $E(k) \neq$ H, O.

For any non-redox system, $2\cdot f(O) - f(H)$ is not a new, independent balance, i.e., it can be presented as a linear combination of charge and elemental/core balances. For this purpose, the balances: $f(O)$, and $f(H)$ and then $2\cdot f(O) - f(H)$, are not applied for description of non-redox systems.

These properties of $2\cdot f(O) - f(H)$ are valid for redox and non-redox systems of any degree of complexity. In other words, this regularity is the criterion distinguishing between redox and non-redox systems [2]. This regularity can be extended on binary solvent [8,9] and mixed-solvent [10] media, in general. The most convenient way of proving the linear relationship between $2\cdot f(O) - f(H)$ and the remaining balances is the reduction to the identity 0 = 0, presented in [11,12].

The statement "any degree of complexity" includes mono- and multi-phase, metastable and non-equilibrium systems [7]. All these (redox and non-redox) systems are resolvable in simulation procedure, with use of iterative computer programs, realized in accordance with the principles of the generalized approach to electrolytic systems (GATES), based on well-established and compatible set of charge and elemental/core balances, and all available thermodynamic knowledge related to the system in question. This knowledge is involved with equilibrium constants values, interrelating some particular species of this system. The knowledge gaining from redox systems is realized through simulations made according to GATES/GEB principles, as a most comprehensive way for studying such systems. The balances and relations for equilibrium constants are algebraic equations. Note that equation-based simulations are most commonly used in physics and related sciences [15].

For a redox system, any linear combination of *pr*-GEB = $2\cdot f(\mathrm{O}) - f(\mathrm{H})$ and the remaining balances is not reducible to the identity 0 = 0, but to the simplest form of GEB, obtained according to Approach II to GEB [11]. The Approach II is equivalent to the Approach I to GEB; the latter is based on card game principle, with players, fans and electrons as money [1]. The Approach I, considered as a "short" version of GEB, needs prior knowledge of oxidation numbers for all elements of the system in question. Such a knowledge is not needed in the Approach II to GEB, where the composition (expressed by chemical formulas) of components forming an electrolytic system and the species formed in this system together with their external charges, are only required. It is the great advantage of the Approach II when applied to formulation of GEB for electrolytic systems with complex organic components and species involved. The complementarity of the Approaches I and II to GEB with other balances was regarded as the Harmony of Nature [16]. Both Approaches will be applied also in the present paper for some dynamic systems represented by titrations, where V mL of titrant (T) is added into V_0 mL of titrand (D), and V_0+V mL of D+T system is obtained, when additivity of the volumes be assumed.

The $2\cdot f(\mathrm{O}) - f(\mathrm{H})$, charge balance and elemental/core balances will be expressed first in terms of the numbers of particular entities. Next, the resulting balances will be presented in terms of molar concentrations, to be fully compatible with expressions for equilibrium constants, presented in terms of molar concentrations of the related species.

2. FORMULATING THE GEB FOR REDOX SYSTEMS – EXAMPLES

Example 1. V mL of titrant composed of $KMnO_4$ (N_{01}) + H_2O (N_{02}) is added into V_0 mL of titrand composed of $MnSO_4$ (N_{03}) + H_2SO_4 (N_{04}) + H_2O (N_{05}). The following species: H_2O (N_1), H^+ (N_2, n_2), OH^- (N_3, n_3), K^+ (N_4, n_4), HSO_4^- (N_5, n_5), SO_4^{2-} (N_6, n_6), MnO_4^- (N_7, n_7), MnO_4^{2-} (N_8, n_8), Mn^{3+} (N_9, n_9), $MnOH^{2+}$ (N_{11}, n_{11}), Mn^{2+} (N_{12}, n_{12}), $MnOH^+$ (N_{13}, n_{13}), $MnSO_4$ (N_{14}, n_{14}), **MnO_2** (N_{15}, n_{15}) present in the system are involved in the balances:

- $f(\mathrm{H})$

$$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + 2N_4n_4 + N_5(1 + 2n_5) + 2N_6n_6 + 2N_7n_7 + 2N_8n_8 + 2N_9n_9 + N_{11}(1 + 2n_{11}) + 2N_{12}n_{12} + N_{13}(1 + 2n_{13}) + 2N_{14}n_{14} + 2N_{15}n_{15} = 2N_{02} + 2N_{04} + 2N_{05} \quad (3)$$

- $f(\mathrm{O})$

$$N_1 + N_2n_2 + N_3(1 + n_3) + N_4n_4 + N_5(4 + n_5) + N_6(4 + n_6) + N_7(4 + n_7) + N_8(4 + n_8) + N_9n_9 + N_{11}(1 + n_{11}) + N_{12}n_{12} + N_{13}(1 + n_{13}) + N_{14}(4 + n_{14}) + N_{15}(2 + n_{15})$$

$$= 4N_{01} + N_{02} + 4N_{03} + 4N_{04} + N_{05} \tag{4}$$

- $2\cdot f(O) - f(H) = pr$-GEB

$$- N_2 + N_3 + 7N_5 + 8N_6 + 8N_7 + 8N_8 + N_{11} + N_{13} + 8N_{14} + 4N_{15} = 8N_{01} + 8N_{03} + 6N_{04} \tag{5}$$

Addition of (5) to charge balance (6) and balances $f(K)$ (7), $6\cdot f(SO_4)$ (8), $4\cdot f(Mn)$ (9)

$$N_2 - N_3 + N_4 - N_5 - 2N_6 - N_7 - 2N_8 + 3N_9 + 2N_{11} + 2N_{12} + N_{13} = 0 \tag{6}$$

$$N_{01} = N_4 \tag{7}$$

$$6N_{03} + 6N_{04} = 6N_5 + 6N_6 + 6N_{14} \tag{8}$$

$$4N_{01} + 4N_{03} = 4N_7 + 4N_8 + 4N_9 + 4N_{11} + 4N_{12} + 4N_{13} + 4N_{14} + 4N_{15} \tag{9}$$

gives

$$2(N_{12} + N_{13} + N_{14}) - (3N_7 + 2N_8 - N_9 - N_{11}) = 2N_{03} - 3N_{01} \tag{10}$$

and then

$$\begin{gathered} 2([Mn^{2+}] + [MnOH^{+}] + [MnSO_4]) - (3[MnO_4^{-}] + 2[MnO_4^{2-}] - [Mn^{3+}] - [MnOH^{2+}]) \\ = (2C_0V_0 - 3CV)/(V_0+V) \end{gathered} \tag{11}$$

where: $C_0V_0 = 10^3\cdot N_{03}/N_A$, $CV = 10^3\cdot N_{01}/N_A$, $[X_i^{z_i}](V_0+V) = 10^3\cdot N_i/N_A$. Moreover, we have $C_{01}V_0 = 10^3\cdot N_{04}/N_A$. Eq. (11) is the simplest/shortest form of the GEB related to this system.

Other intentional, linear combinations are also possible. One of them is used to prove directly the equivalency of the Approaches I and II to GEB. When adding Eqs. (5) - (8), we obtain the equation

$$7N_7 + 6N_8 + 4N_{15} + 3(N_9 + N_{11}) + 2(N_{12} + N_{13} + N_{14}) = 7N_{10} + 2N_{30} \tag{12}$$

Subtraction of Eq. (12) from $Z_{Mn}f(Mn)$ (13) ($Z_{Mn}=25$)

$$Z_{Mn}\cdot(N_7 + N_8 + N_{15} + N_9 + N_{11} + N_{12} + N_{13} + N_{14}) = Z_{Mn}\cdot N_{10} + Z_{Mn}\cdot N_{30} \tag{13}$$

gives

$$\begin{gathered} (Z_{Mn}-7)N_7 + (Z_{Mn}-6)N_8 + (Z_{Mn}-4)N_{15} + (Z_{Mn}-3)(N_9 + N_{11}) + (Z_{Mn}-2)(N_{12} + N_{13} + N_{14}) \\ = (Z_{Mn}-7)N_{10} + (Z_{Mn}-2)N_{30} \end{gathered} \tag{14}$$

and then

$$\begin{gathered} (Z_{Mn}-7)[MnO_4^{-}] + (Z_{Mn}-6)[MnO_4^{2-}] + (Z_{Mn}-4)[\mathbf{MnO_2}] + (Z_{Mn}-3)([Mn^{3+}] + [MnOH^{2+}]) \\ + (Z_{Mn}-2)([Mn^{2+}] + [MnOH^{+}] + [MnSO_4]) = ((Z_{Mn}-7)CV + (Z_{Mn}-2)C_0V_0)/(V_0+V) \end{gathered} \tag{15}$$

Eq. (15) is identical with the one obtained for the related system according to the Approach I to GEB.

Example 2. V_0 mL of titrand (D), containing $Na_2C_2O_4$ (C_0) + H_2SO_4 (C_{01}) + Na_2CO_3 (C_{02}) + CO_2 (C_{03}), is titrated with V mL of titrant T, containing $KMnO_4$ (C) + CO_2 (C_1).

The titrand D is composed of $Na_2C_2O_4$ (N_{01}) + Na_2CO_3 (N_{02}) + CO_2 (N_{03}) + H_2O (N_{04}) + H_2SO_4 (N_{05}), and the titrant T is composed of $KMnO_4$ (N_{06}) + CO_2 (N_{07}) + H_2O (N_{08}), at defined point of titration. The components of this system are as follows:

H_2O (N_1), H^+ (N_2, n_2), OH^- (N_3, n_3), Na^+ (N_4, n_4), H_2CO_3 (N_5, n_5), HCO_3^- (N_6, n_6), CO_3^{2-} (N_7, n_7), $H_2C_2O_4$ (N_8, n_8), $HC_2O_4^-$ (N_9, n_9), $C_2O_4^{2-}$ (N_{11}, n_{11}), HSO_4^- (N_{12}, n_{12}), SO_4^{2-} (N_{13}, n_{13}), MnO_4^- (N_{14}, n_{14}), MnO_4^{2-} (N_{15}, n_{15}), Mn^{3+} (N_{16}, n_{16}), $MnOH^{2+}$ (N_{17}, n_{17}), Mn^{2+} (N_{18}, n_{18}), $MnOH^+$ (N_{19}, n_{19}), $MnSO_4$ (N_{21}, n_{21}), K^+ (N_{22}, n_{22}).

From the elemental balances

- $f(H)$

$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + 2N_4n_4 + N_5(2 + 2n_5) + N_6(1 + 2n_6) + 2N_7n_7 + N_8(2 + 2n_8) + N_9(1 + 2n_9) + 2N_{11}n_{11} + N_{12}(1 + 2n_{12}) + 2N_{13}n_{13} + 2N_{14}n_{14} + 2N_{15}n_{15} + 2N_{16}n_{16} + N_{17}(1 + 2n_{17}) + 2N_{18}n_{18} + N_{19}(1 + 2n_{19}) + 2N_{21}n_{21} + 2N_{22}n_{22} = 2N_{04} + 2N_{05} + 2N_{08}$ (16)

- *f*(O)

$N_1 + N_2n_2 + N_3(1 + n_3) + N_4n_4 + N_5(3 + n_5) + N_6(3 + n_6) + N_7(3 + n_7) + N_8(4 + n_8) + N_9(4 + n_9) + N_{11}(4 + n_{11}) + N_{12}(4 + n_{12}) + N_{13}(4 + n_{13}) + N_{14}(4 + n_{14}) + N_{15}(4 + n_{15}) + N_{16}n_{16} + N_{17}(1 + n_{17}) + N_{18}n_{18} + N_{19}(1 + n_{19}) + N_{21}(4 + n_{21}) + N_{22}n_{22}$

$= 4N_{01} + 3N_{02} + 2N_{03} + N_{04} + 4N_{05} + 4N_{06} + 2N_{07} + N_{08}$ (17)

we have

- $2\cdot f(\mathrm{O}) - f(\mathrm{H})$

$- N_2 + N_3 + 4N_5 + 5N_6 + 6N_7 + 6N_8 + 7N_9 + 8N_{11} + 7N_{12} + 8N_{13} + 8N_{14} + 8N_{15} + N_{17} + N_{19} + 8N_{21} = 8N_{01} + 6N_{02} + 4N_{03} + 6N_{05} + 8N_{06} + 4N_{07}$ (18)

Eq. (18) is the primary form of the related GEB, $2\cdot f(\mathrm{O}) - f(\mathrm{H})$ = *pr*-GEB. Adding (18) to charge balance (19) and elemental balances: *f*(Na) (20), *f*(K) (21) and $6\cdot f$(S) (22), $4\cdot f$ (C) (23), $2\cdot f$ (Mn) (24):

$N_2 - N_3 + N_4 - N_6 - 2N_7 - N_9 - 2N_{11} - N_{12} - 2N_{13} - N_{14} - 2N_{15} + 3N_{16}$

$+ 2N_{17} + 2N_{18} + N_{19} + N_{22} = 0$ (19)

$2N_{01} + 2N_{02} = N_4$ (20)

$N_{06} = N_{22}$ (21)

$6N_{05} = 6N_{12} + 6N_{13} + 6N_{21}$ (22)

$8N_{01} + 4N_{02} + 4N_{03} + 4N_{07} = 4N_5 + 4N_6 + 4N_7 + 8N_8 + 8N_9 + 8N_{11}$ (23)

$2N_{06} = 2N_{14} + 2N_{15} + 2N_{16} + 2N_{17} + 2N_{18} + 2N_{19} + 2N_{21}$ (24)

we get, by turns:

$2N_{01} + 5N_{14} + 4N_{15} + N_{16} + N_{17} = 2N_8 + 2N_9 + 2N_{11} + 5N_{06}$ (25a)

$2(N_8 + N_9 + N_{11}) - (5N_{14} + 4N_{14} + N_{16} + N_{17}) = 2N_{01} - 5N_{06}$ (25b)

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

$= (2C_0V_0 - 5CV)/(V_0+V)$ (26)

where the formulae: $C_0V_0 = 10^3\cdot N_{01}/N_A$, $CV = 10^3\cdot N_{06}/N_A$, $[X_i^{z_i}](V_0+V) = 10^3N_i/N_A$ were applied. It is assumed that a due excess of H_2SO_4 is added and the titrand is heated before the titration for the reaction to proceed.

The respective multipliers in the balances (19) – (24) were intentionally selected such that the resulting GEB for the system assumes its simplest form, containing minimal number of components, where all “fans” were cancelled. Among others, carbonate species: those resulting from oxidation of oxalate and those present as CO_2 and carbonate, are absent in Eq. (26). However, the balance (18) and any combination of (18) with one or more (charge, elemental) balances is fully equivalent to Eq. (26), i.e., all them fulfill the properties of GEB.

One can also prove that Eq. (26) results from the Approach I to GEB, related to the system in question. Denoting atomic numbers for C and Mn by Z_C (=6) and Z_{Mn} (=25), according to the Approach I to GEB, we get

$2(Z_C-3)([H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]) + Z_C([H_2CO_3] + [HCO_3^-] + [CO_3^{2-}])$

$+ (Z_{Mn}-7)[MnO_4^-] + (Z_{Mn}-6)[MnO_4^{2-}] + (Z_{Mn}-3)([Mn^{3+}] + [MnOH^{2+}]) + (Z_{Mn}-2)([Mn^{2+}] + [MnOH^+] + [MnSO_4]) = 2(Z_C-3)C_0V_0/(V_0+V) + (Z_C-4)(C_{02}V_0 + C_{03}V_0 + C_1V)/(V_0+V)$
$+ (Z_{Mn}-7)CV/(V_0+V)$ (27)

Eq. (27) is equivalent to Eq. (26). Subtracting from Eq. (27) the sum of balances obtained after multiplication of concentration balances for C and Mn by (Z_C-4) and $(Z_{Mn}-2)$ resp., we get Eq. (26); this proves the equivalency of the Approaches I and II to GEB.

3. COMPLETING THE BALANCES FOR REDOX SYSTEMS

The set of material balances involves all real species of a system in question. Particularly, the generalised electron balance (GEB) concept completes the set of balances referred to redox systems. Ultimately, all the balances of the system are expressed in terms of concentrations.

In Example 2, the GEB, expressed by Eq. (26) or Eq. (27), is completed by the charge balance

$[H^+] – [OH^-] + [Na^+] – [HCO_3^-] – 2[CO_3^{2-}] – [HC_2O_4^-] – [HSO_4^-] – 2[SO_4^{2-}] – [MnO_4^-] – 2[MnO_4^{2-}] + 3[Mn^{3+}] + 2[MnOH^{2+}] + 2[Mn^{2+}] + [MnOH^+] + [K^+] = 0$ (19a)

obtained from Eq. (19), and a set of concentration balances

$[Na^+] = 2(C_0 + C_{01})V_0/(V_0+V)$ (20a)

$[K^+] = CV/(V_0+V)$ (21a)

$[HSO_4^-] + [SO_4^{2-}] + [MnSO_4] = C_{01}V_0/(V_0+V)$ (22a)

$[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + 2[H_2C_2O_4] + 2[HC_2O_4^-] + 2[C_2O_4^{2-}]$
$= (2C_0V_0 + C_{02}V_0 + C_{03}V_0 + C_1V)/(V_0+V)$ (23a)

$[MnO_4^-] + [MnO_4^{2-}] + [Mn^{3+}] + [MnOH^{2+}] + [Mn^{2+}] + [MnOH^+] + [MnSO_4] = CV/(V_0+V)$ (24a)

obtained from Eqs. (20) – (24) for *f*(Na), *f*(K), *f*(S), *f* (C), and *f* (Mn).

As we see, $[Na^+]$ and $[K^+]$ enter the balances (20a) and (21a) as the sole components. Concluding, at defined C, C_0, C_{02} and V_0 values, $[Na^+]$ (Eq. (20a)) and $[K^+]$ (Eq. (21a)) enter the charge balance (Eq. (19a)) as numbers, at defined V-value, and therefore, they are not formally considered as equations. Generalizing, the material balance involving one species is not termed as concentration balance, when perceived form the viewpoint of solving the set of algebraic equations. The term “concentration balance” is ascribed to the balance involving at least two species; in Example 2, this criterion is fulfilled by k=3 concentration balances, expressed by Eqs. (22a) – (24a). Together with equations (19a) and (26) (or (27)), there are k+2 = 5 balances. In calculations, the volume V of titrant T is considered as the control variable, with constant value at defined step of the simulated titration.

4. COMPLETING THE SET OF EQUILIBRIUM CONSTANTS

Concentrations of the species involved in charge, concentration balances and GEB presented in Example 2 (see Eqs. (19a) – (24a) and (26)), are interrelated in expressions for the corresponding equilibrium constants [6]:

$[HC_2O_4^-] = 10^{pH-1.25}\cdot[H_2C_2O_4]$, $[C_2O_4^{2-}] = 10^{pH-4.27}\cdot[HC_2O_4^-]$, $[HCO_3^-] = 10^{pH-6.3}\cdot[H_2CO_3]$,
$[CO_3^{2-}] = 10^{pH-10.1}\cdot[HCO_3^-]$, $[SO_4^{2-}] = 10^{pH-1.8}\cdot[HSO_4^-]$, $[MnOH^{2+}] = 10^{pH-0.2}\cdot[Mn^{3+}]$,
$[MnSO_4] = 10^{2.28}\cdot[Mn^{2+}][SO_4^{2-}]$, $[MnO_4^-] = 10^{5A(E-1.507)+8pH}\cdot[Mn^{2+}]$,
$[MnO_4^-] = 10^{A(E-0.56)}\cdot[MnO_4^{2-}]$, $[Mn^{3+}] = 10^{A(E-1.509)}\cdot[Mn^{2+}]$, $[H_2CO_3] = 10^{A(E+0.386)}\cdot[H_2C_2O_4]^{0.5}$
where $pH = -\log[H^+]$, $1/A = (RT/F)\cdot\ln 10$, F – Faraday constant, R – gas constant, T – temperature [K]; A = 16.92 at 298 K. As we see, $[Na^+]$ and $[K^+]$ are not involved in the set of equilibrium constants (see the comment above).

It is assumed that the solution in the redox system is sufficiently acidified (H_2SO_4) to prevent formation of **MnO_2**, i.e., the system is homogeneous (solution) during the titration, and thus **MnO_2** is not involved in the balance (24a), [**MnO_2**] = 0. It is also assumed that the solubility product for **MnC_2O_4** is not crossed, i.e., [**MnC_2O_4**] = 0.

5. CHOICE OF INDEPENDENT VARIABLES AND OPTIMIZATION PROCEDURE

The choice of independent variables within GATES/GEB is made for optimization/minimization purposes, according to certain rules. For a system characterized by k concentration balances, derived from elemental/core balances (≠ H, O), we have k+2 independent, scalar variables, represented by a vector **x** of these variables

$$\mathbf{x}^T = (pX_1,...,pX_k, E, pH) \qquad (^T\text{ – transposition sign}) \tag{28}$$

The number k+2 of components of the vector **x** is equal to the number of balances; the two other balances are, of course, GEB and charge balance. Total number of balances equal to the number of independent variables ensures unambiguity of solutions – both in static, and in dynamic systems. In the dynamic systems, represented by titration, we have the volume V of titrant as a control variable. There is not an additional, (k+3)th variable in the system, because the independent variables are calculated at a fixed – at the given moment – V-value, **x** = **x**(V). The independent variables are the variables in negative powers in exponents of the relevant concentrations. Then we have:

$$[e^-] = 10^{-A\cdot E} \tag{29}$$

(in hydrogen scale) or

$$[e^-] = 10^{-A\cdot(E+E^o)} \tag{30}$$

(in absolute scale, E^o = 4.44 V) [17,18], $[H^+] = 10^{-pH}$, $[X_i] = 10^{-pX_i}$. Each concentration balance is represented by one variable, GEB is represented by E variable, charge balance – by pH variable; this is the most natural allocation criterion. The fact that all the variables chosen are put in exponents (with a base 10) means that all the variables are in the 'homogenized' scale. It also causes that the balances are considered as the system of nonlinear algebraic equations.

All the balances can be rewritten into the form of equations $F_i(\mathbf{x}(V)) = 0$ (i = 1,…,k+2), zeroing the sum of squares, SS, i.e.,

$$SS = SS(V) = \sum_{i=1}^{k+2}[F_i(\mathbf{x}(V))]^2 = 0 \tag{31}$$

for different V-values, if the correct values of variables: $pX_1(V)$,…, $pX_k(V)$, E(V), pH(V) forming the vector **x**(V) in Eq. (31) are chosen properly.

In the minimization procedure, the correct values of the variables at defined V-values are not known *a priori*. Therefore, the iterative procedure should start at certain numerical values (starting values, s) for each variable in $\mathbf{x}_{(s)}(V)$. For these values of the variables

$$SS_{(s)}(V) = \sum_{i=1}^{k+2} [F_i(x_{(s)}(V))]^2 > 0 \tag{32}$$

To improve the optimization procedure, we select the starting value $V = V_{(s)}$ from this range of the titration curve, where the choice of starting values $pX_{1(s)}(_{(s)}),\ldots, pX_{k(s)}(V_{(s)}), E_{(s)}(V_{(s)}), pH_{(s)}(V_{(s)})$ for each variable ($pX_1,\ldots, pX_k$, E, pH) does not cause serious problems. When (some of) the values $pX_{1(s)}(_{(s)}),\ldots, pX_{k(s)}(V_{(s)}), E_{(s)}(V_{(s)}), pH_{(s)}(V_{(s)})$ are too distant from the true values, the optimization procedure may not start.

When the iterative procedure starts at a positive step for V assumed, $\Delta V > 0$, then the values for variables obtained at the volume V_j, i.e. $\mathbf{x}(V_j)$, are the starting values for these variables assessed at $V_j + \Delta V$, etc. The iterations are carried out, up to a pre-assumed, final value for V. Within a jump region on the titration curve, the step ΔV is usually (sometimes: gradually) diminished, and after the exit from the jump region, a value of the step is increased again. After receiving/collecting the results for higher V-values, we start again from the initial starting point, i.e. $V_{(s)}$, but with a negative step, $-\Delta V$. The results obtained for lower V-values, up to a point close to V = 0, after reversing the order of rows, sticks together with the results obtained for higher V-values; an ordered output file is thus obtained.

In the columns of the corresponding output file, concentrations of other components, not directly related to the primary variables, are also recorded. Those concentrations are obtained from the respective dependencies resulting from expressions for equilibrium constants; e.g., $[MnO_4^-] = 10^{5A\cdot(E-1.507)+8pH-pMn}$. The concentrations of various components are then used for construction of speciation diagrams, where logarithms of these concentrations are recorded on the ordinate.

The iterative procedure for any V-value is completed if the resulting differences in SS(V) related to consecutive iterations, namely: $SS_{(j)}(V)$ and $SS_{(j+1)}(V)$ are smaller than a predefined, sufficiently small value $\delta > 0$, i.e., $|SS_{(j)}(V) - SS_{(j+1)}(V)| < \delta$. At the same time, the value of $SS_{(j+1)}(V)$ must be sufficiently close to zero, $SS_{(j+1)}(V) \cong 0$. In the calculations made here and elsewhere, the $SS_{(j+1)}(V)$ values, where the calculations were ended, are ca. $10^{-30} - 10^{-31}$.

6. ITERATIVE COMPUTER PROGRAM

The independent variables, related to the system presented in Example 2, can be characterized by the vector

$$\mathbf{x}^T = (pH_2C_2O_4, pMn, pSO_4, E, pH) \tag{33}$$

where $pH_2C_2O_4 = -\log[H_2C_2O_4]$, $pMn = -\log[Mn^{2+}]$, $pSO_4 = -\log[SO_4^{2-}]$. One can state that the number of fundamental variables (Eq. (33)) equals to the number of balances (k = 3+2 = 5).

The independent variables determined at particular V-value enable to know the concentration of any other species at this V-value. The collected data $\mathbf{x}(V)$ found from calculations made at different

V-values enable to plot the curves in 2D scale or areas in 3D scale. For the system presented in Example 2, it is advisable to apply the fraction titrated

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \tag{34}$$

on the abscissa of the related graphs, where $C_0 \cdot V_0$ is the number of mmoles of the analyte A in titrand (D), and $C \cdot V$ is the number of mmoles of titrant (T) added to D, up to a given point of the titration process. The iterative computer programs are presented in Appendix 1 (for Example 1) and Appendix 2 (for Example 2). In computer programs related to these systems it were assumed that $[MnO_2] = 0$. The output files in Excel are attached under the link.

7. GRAPHICAL PRESENTATION OF RESULTS

The results of calculations are presented graphically in Figures 1 and 2a,b for Example 1 (at V_0=10, C_0=0.01, C_{01}=1, C=0.02), and in Figures 3a,b, 4a,b and 5 for Example 2 (at V_0=10, C_0=0.01, C_{01}=1.0, C_{02}=0, C_{03}=C_1= 0.001, C=0.02).

Ad. Example 1. After addition of $KMnO_4$ solution into a sufficiently acidified (H_2SO_4) solution of $MnSO_4$, synproportionation to **MnO_2** does not occur; i.e., a solubility product for **MnO_2** (see Section 9) is not crossed. There is, however, a noticeable synproportionation, associated with the formation of Mn^{3+} and $MnOH^{2+}$, described by the reaction equations:

$$4Mn^{2+} + MnO_4^- + 8H^+ = 5Mn^{3+} + 4H_2O \tag{35}$$

$$4Mn^{2+} + MnO_4^- + 3H^+ + H_2O = 5MnOH^{2+} \tag{36}$$

$$4MnSO_4 + MnO_4^- + 12H^+ = 5Mn^{3+} + 4HSO_4^- + 4H_2O \tag{37}$$

$$4MnSO_4 + MnO_4^- + 7H^+ + H_2O = 5MnOH^{2+} + 4HSO_4^- \tag{38}$$

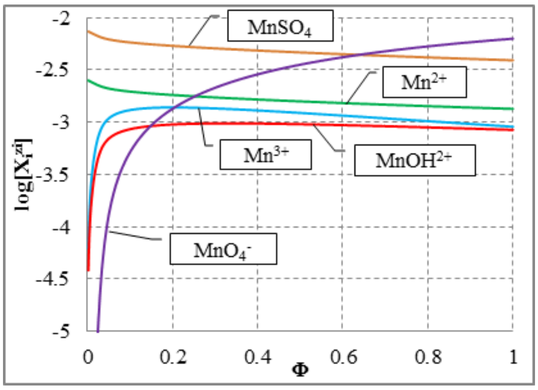


Figure 1. Speciation diagram for Example 1. For details – see text.

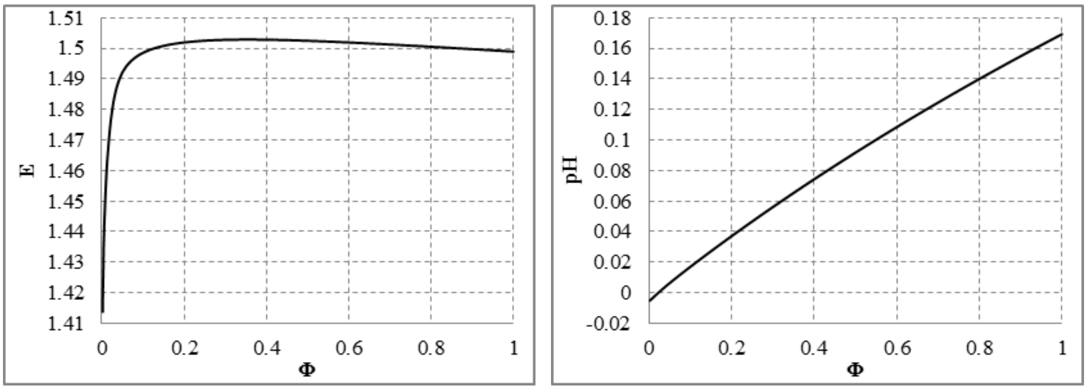
In these equations, the dominant species were taken into account. A small yield of the synproportionation reaction is evidenced by the fact that the species introduced by the titrand (mainly: Mn^{2+} and $MnSO_4$) and titrant (MnO_4^-) dominate in the whole Φ-range. The concentrations of $MnOH^+$

and MnO_4^{2-} are very low; at $\Phi = 1$ we have: $\log[MnOH^+] = -13.30$ and $\log[MnO_4^{2-}] = -18.09$. Potential E in the system passes through a flat maximum at Φ ca. 0.35, and then decreases (Fig. 2a). The titrand is strongly buffered; a small pH-change is affected by dilution effect and the fact, that the reactions (35) - (38) occur to a small extent.

Ad. Example 2. The oxidation of $H_2C_2O_4$ in manganometric titration occurs according to the scheme,

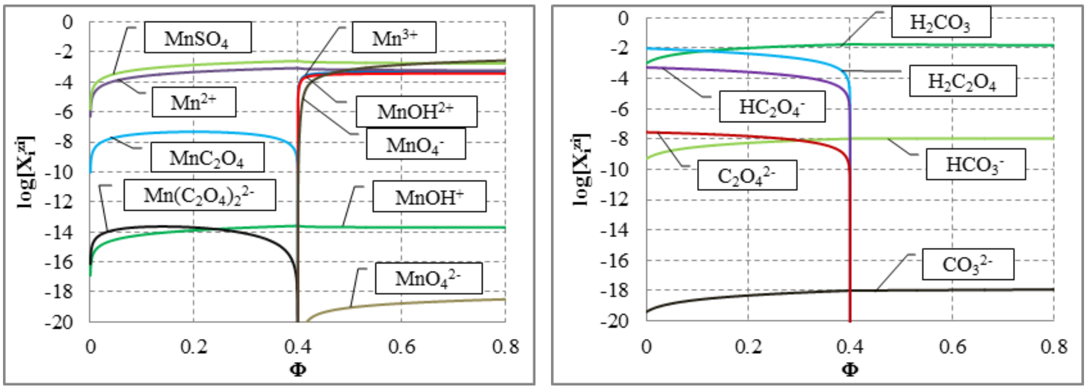
$$5H_2C_2O_4 + 2MnO_4^- + 2HSO_4^- + 4H^+ + 2H_2O = 10H_2CO_3 + 2MnSO_4 \quad (39)$$

where predominating species are involved (Fig. 3a,b); $MnSO_4$ is the related sulfate complex, $[MnSO_4] > [Mn^{2+}]$. The stoichiometry of this reaction, equal 2 : 5 = 0.4, corresponds to the Φ value at the equivalent (eq) point, where abrupt growth in potential (E) value occurs (Fig. 4a), $\Phi_{eq} = CV_{eq}/(C_0V_0) = 0.4$, where V_{eq} is the equivalent volume, see Table 1. The small change in pH value (Fig. 4b) is involved with a high buffer capacity of the titrand D, and affected significantly by dilution effect, not only by reaction (39), where protons are attached (compare with [6]).



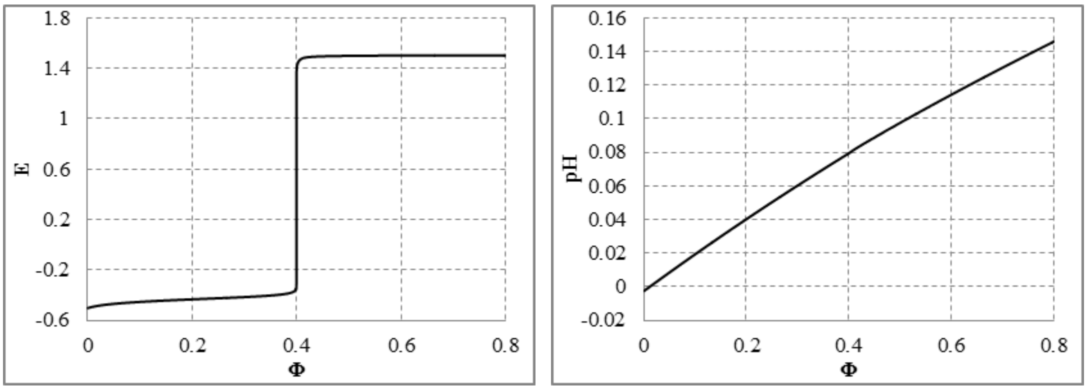
(2a) (2b)

Figure 2. The relationships: (2a) E vs. Φ; (2b) pH vs. Φ for Example 1. For details – see text.



(3a) (3b)

Figure 3. Speciation diagrams for (3a) Mn-species; (3b) C-species for Example 2. For details – see text.



(4a) (4b)

Figure 4. The relationships: (4a) E vs. Φ; (4b) pH vs. Φ for Example 2. For details – see text.

Concentration of CO_2 formed in this system exceeds the solubility of CO_2 in strongly acidified aqueous media [19,20]. To keep/retain CO_2 dissolved in water as H_2CO_3, we should virtually assume that the electrolytic system consists only from the liquid phase, i.e., gaseous phase does not enter the system composition. Moreover, [**MnO_2**] = 0 and [**MnC_2O_4**] = 0 in this system. For the precipitate of **MnC_2O_4**, it can be stated by tracking the values of $q = [Mn^{2+}][C_2O_4^{2-}]/K_{sp} < 1$ (Fig. 5), where $K_{sp} = 10^{-5.3}$ is the solubility product for this precipitate. **MnC_2O_4** in Fig. 3a relates to soluble complex. Let us also notice (Fig. 3a) that just after crossing the equivalent point we have $[Mn^{3+}] + [MnOH^{2+}] > [MnO_4^-]$.

The (hydrated) electron e^- [21-23] is formally an ion, and – as such – it should enter the charge balance. The points for $\Phi < \Phi_{eq} = 0.4$ on the titration curve $E = E(\Phi)$ (Fig. 4a, Table 1) correspond to $E < 0$, when E is calculated in standard hydrogen electrode (SHE) scale, Eq. (29). In particular, $E < 0$ correspond to abnormally high values for $[e^-]$ [17,18]. However, when applying Eq. (30), the $[e^-]$ value is low; e.g., for E = –0.5 V we have extremely low value $[e^-] = 10^{-16.92\cdot(-0.5+4.44)} = 2.16\cdot10^{-67}$, and then omission of $[e^-]$ in Eq. (37a) is justified, within the SS-value ca. 10^{-30} expressing the degree of fit (Eq. 31).

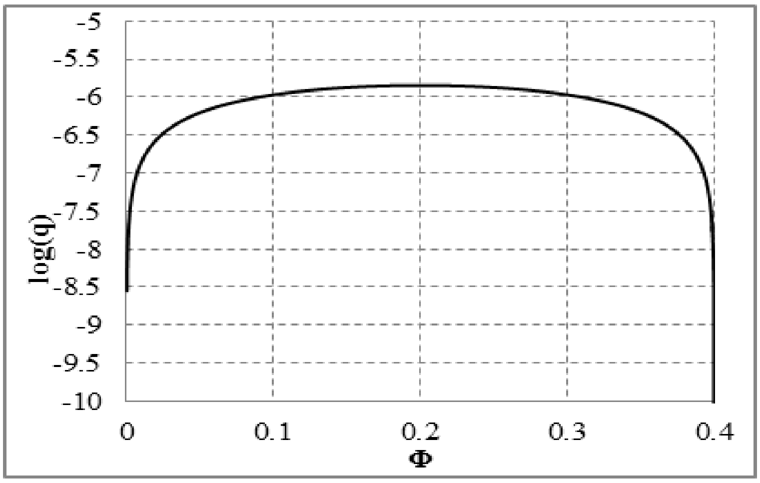


Figure 5. The log(q) vs. Φ relationship for **MnC_2O_4** in Example 2. For details – see text.

8. ON THE COMPLETENESS OF EQUILIBRIUM DATA

One of the numerous, valuable opportunities offered by GATES and GATES/GEB in particular, is the possibility to carry out the "variations on the subject" [7,24-27], where we try to know what would happen, if some constraints put on a metastable system will be removed and the reaction be conducted in a thermodynamic manner, in accordance with the conditions imposed by the equilibrium constants. For example, one can also check the changes of measurable variables, e.g. potential E, if we arbitrarily assume some unknown *a priori* values for the corresponding equilibrium constants, e.g., stability constants of pre-assumed complexes $Mn(SO_4)_i^{+3-2i}$ [7]. One can also check the course of reactions when concentrations of some components in the system will be changed [3].

Table 1. Change in potential E values in the vicinity of equivalent (eq) point for the system in Example 2.

Φ	E [V]
0.3900	-0.3805
0.3950	-0.3714
0.3980	-0.3594
0.3990	-0.3505
0.3992	-0.3476
0.3994	-0.3439
0.3996	-0.3387
0.3998	-0.3298
0.4000	-0.2144
0.4002	1.3761
0.4004	1.3939
0.4006	1.4044
0.4008	1.4118
0.4010	1.4176
0.4020	1.4356
0.4050	1.4597
0.4100	1.4761

However, the possibilities of "variations on the subject" may be limited by incomplete physiochemical knowledge about the system in question. In Examples 1 and 2, the matter lies in a lack of knowledge related to the solubility product of **MnO_2** precipitate.

One can recall that the precipitation of **MnO_2** as the product of MnO_4^- reduction is possible e.g. in manganometric titration of $FeSO_4$ solution [28-30], if H_2SO_4 is absent or added in insufficient quantities. Under such conditions, the precipitation of **$Fe(OH)_3$** is also possible: $MnO_4^- + 3Fe^{2+} + 7H_2O = \mathbf{MnO_2} + 3\mathbf{Fe(OH)_3} + 5H^+$.

9. ON THE CONSISTENCY OF EQUATIONS

The set of algebraic equations should be consistent, i.e., non-contradictory. Inconsistency of equations can result from different reasons. The first is the inconsistency between the values of the equilibrium constants. The values of the equilibrium constants are obtained experimentally, and therefore they are subjected to errors of different kind. Namely, the equilibrium constants are determined by using different models, different measurement methods, made at different temperatures and/or ionic strengths, or referenced to different chemical reactions. Therefore, the physicochemical data found in scientific literature are not compatible, as a rule. What is more, these data are often incomplete. On the other hand, the tables of equilibrium constants are usually characterized by the redundancy, i.e., (apparent) excess of data; these data can be contradictory to each other. Examples of this type are cited, *inter alia*, in [11]. It follows from there that $E_{01} = 1.69$ V for $MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$, $E_{02} = 2.26$ V for $MnO_4^{2-} + 4H^+ + 2e^- = MnO_2 + 2H_2O$, and $E_{03} = 0.56$ V for $MnO_4^- + e^- = MnO_4^{2-}$ are incompatible; $E_{02} - E_{01} = 0.57 \neq E_{03}$.

Even very small differences in the equilibrium constants (much less than the experimental error), resulting from the placement of the corresponding equilibrium constants in various relationships, lead to inconsistency [11]. Inconsistent equilibrium constant lead to contradictions between the appropriate equations, and therefore it is impossible to solve these equations. The equilibrium constants used for calculations may be false/not correct; the thing is that they must be consistent. This is the “Iron Rule” of mathematics, obligatory also in the calculations related to electrolytic systems, based on algebraic operations.

It must be stressed that the GATES [7] is the intrinsically consistent theory, joining fundamental laws of physics and chemistry. Mathematical formalism of these systems arises from three laws: law of charge conservation, law of elements conservation, and law of mass action. GEB is derived from the common root of the elements conservation and then is fully compatible with concentration/core balances, and with charge balance. All the laws impose some initial assumptions about the systems analyzed. These assumptions are inherent in mathematical formalism, expressed in an algorithm applied for calculation purposes, and specified in Appendices I and II.

10. CONCLUSIONS

Computer simulations of scientific experiments are carried out in order to obtain qualitative and quantitative information on the system tested. It particularly concerns titration in dynamic redox D+T system, resulting from gradual addition of a titrant (T) to the titrand (D). All attainable physicochemical knowledge on the system in question can be involved in the algorithm prepared for this purpose.

In this paper, the simulated titrations of acidified (H_2SO_4) solutions of (1) $MnSO_4$, and (2) $H_2C_2O_4$ with a solution of $KMnO_4$ are considered. These systems are described with a set of nonlinear equations, expressed by the GEB, charge and concentration balances. The relationships between the concentrations of the species included in these balances are expressed by complete set of appropriate equilibrium constants. The set of equations is solved using iterative computer programs. On the basis of output files, the graphs of E = E(Φ), pH = pH(Φ) relationships (Eq. 34), and speciation diagrams were obtained. Other relationships are also presented in this work. The data obtained allow to evaluate, from thermodynamic viewpoint, the conditions of the related analyzes and see the details invisible in real titrations. The paper illustrates the advantages inherent in GATES/GEB.

11. FINAL COMMENTS

The thermodynamic approach, involved with computer simulation of two redox systems associated with manganometric titration, is presented. The appropriate functional dependencies, resulting from calculations carried out on the basis GATES/GEB [7], with use of an iterative computer program MATLAB, are the basis of quantitative, physicochemical and analytical considerations (Example 2). Some details involved with the calculation procedure are presented and the computer programs are attached, for better comprehension of executive details inherent in GATES/GEB. It was pointed out, inter alia, to the question of inconsistency of equilibrium constants and the resulting contradiction of the relevant algebraic equations.

The work provides another example of the possibilities offered by GATES/GEB, which is the most perfect tool to obtain information about the thermodynamics of redox systems, on the basis of balances and equilibrium constants values.

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Appendix 1

```
function F = Function_KMnO4_MnSO4(x)

global V Vmin Vstep Vmax V0 C C0 C01 fi H OH pH E Kw pKw A
global Mn7O4 Mn6O4 HSO4 SO4 K
global logMn7O4 logMn6O4 logHSO4 logSO4 logK
global Mn2 Mn2OH Mn2SO4 Mn3 Mn3OH
global logMn2 logMn2OH logMn2SO4 logMn3 logMn3OH

pH=x(1);
E=x(2);
```

```
Mn2=10.^-x(3);
SO4=10.^-x(4);

H=10.^-pH;
pKw=14;
Kw=10.^-14;
OH=Kw./H;
A=16.92;
ZMn=25;

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

Mn7O4=Mn2.*10.^(5.*A.*(E-1.507)+8.*pH);
Mn6O4=10.^(A.*(0.56-E)).*Mn7O4;

Mn2OH=10.^3.4.*Mn2.*OH;
Mn2SO4=10.^2.28.*Mn2.*SO4;

Mn3=Mn2.*10.^(A.*(E-1.509));
Mn3OH=10.^(pH-0.2).*Mn3;

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

   %Charge balance
F=[(H-OH+K-HSO4-2.*SO4-Mn7O4-2.*Mn6O4...
   +3.*Mn3+2.*Mn3OH+2.*Mn2+Mn2OH);

   %Concentration balance of Mn
  (Mn7O4+Mn6O4+Mn3+Mn3OH+Mn2+Mn2OH+Mn2SO4-(C0.*V0+C.*V)./(V0+V));

   %Concentration balance of S
   (HSO4+SO4+Mn2SO4-(C0+C01).*V0./(V0+V));

   %Electron balance
   ((ZMn-7).*Mn7O4+(ZMn-6).*Mn6O4+(ZMn-3).*(Mn3+Mn3OH)...
   +(ZMn-2).*(Mn2+Mn2OH+Mn2SO4)-((ZMn-2).*C0.*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);
logHSO4=log10(HSO4);
logSO4=log10(SO4);
logK=log10(K);
% The end of program
```

Appendix 2

```
function F = Function_KMnO4_Na2C2O4(x)

global V Vmin Vstep Vmax V0 C C1 C0 C01 C02 fi H OH pH E Kw pKw A aa
global H2C2O4 HC2O4 C2O4 H2CO3 HCO3 CO3 K
global logH2C2O4 logHC2O4 logC2O4 logH2CO3 logHCO3 logCO3 logK
global Mn7O4 Mn6O4 HSO4 SO4 Na
global logMn7O4 logMn6O4 logHSO4 logSO4 logNa
global Mn3 Mn3OH Mn3C2O4 Mn3C2O42 Mn3C2O43
global logMn3 logMn3OH logMn3C2O4 logMn3C2O42 logMn3C2O43
global Mn2 Mn2OH Mn2SO4 Mn2C2O4 Mn2C2O42
global logMn2 logMn2OH logMn2SO4 logMn2C2O4 logMn2C2O42
global pr logpr q logq

pH=x(1);
E=x(2);
if aa==0
   Mn2=10.^-x(3);
   pr=0;
else
   pr=10.^-x(3);
end;
H2C2O4=10.^-x(4);
SO4=10.^-x(5);

H=10.^-pH;
pKw=14;
Kw=10.^-14;
OH=Kw./H;
A=16.92;
ZMn=25;
ZC=6;
Kso=10.^-5.3;

HC2O4=10.^(pH-1.25).*H2C2O4;
C2O4=10.^(pH-4.27).*HC2O4;
H2CO3=10.^(A.*(E+0.386)).*H2C2O4.^0.5;
HCO3=10.^(pH-6.3).*H2CO3;
CO3=10.^(pH-10.1).*HCO3;

if aa==1
   Mn2=Kso./C2O4;
end;

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

Mn7O4=Mn2.*10.^(5.*A.*(E-1.507)+8.*pH);
Mn6O4=10.^(A.*(0.56-E)).*Mn7O4;

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

```
Mn2SO4=10.^2.28.*Mn2.*SO4;
Mn2C2O4=10.^3.82.*Mn2.*C2O4;
Mn2C2O42=10.^5.25.*Mn2.*C2O4.^2;

Mn3=Mn2.*10.^(A.*(E-1.509));
Mn3OH=10.^(pH-0.2).*Mn3;
Mn3C2O4=10.^9.98.*Mn3.*C2O4;
Mn3C2O42=10.^16.57.*Mn3.*C2O4.^2;
Mn3C2O43=10.^19.42.*Mn3.*C2O4.^3;

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

   %Charge balance
F=[(H-OH+K+Na-HSO4-2.*SO4-HC2O4-2.*C2O4-HCO3-2.*CO3-Mn7O4-2.*Mn6O4...
   +3.*Mn3+2.*Mn3OH+Mn3C2O4-Mn3C2O42-3.*Mn3C2O43+2.*Mn2+Mn2OH...
   -2.*Mn2C2O42);

   %Concentration balance of Mn
  (Mn7O4+Mn6O4+Mn3+Mn3OH+Mn3C2O4+Mn3C2O42+Mn3C2O43...
   +Mn2+Mn2OH+Mn2SO4+Mn2C2O4+Mn2C2O42+aa.*pr-C.*V./(V0+V));

   %Concentration balance of C
  (2.*H2C2O4+2.*HC2O4+2.*C2O4+H2CO3+HCO3+CO3+2.*Mn2C2O4...
  +4.*Mn2C2O42+2.*Mn3C2O4+4.*Mn3C2O42+6.*Mn3C2O43...
   +2.*aa.*pr-(2.*C0.*V0+C02.*V0+C1.*V)./(V0+V));

   %Concentration balance of S
   (HSO4+SO4+Mn2SO4-C01.*V0./(V0+V));

   %Electron balance
   ((ZMn-7).*Mn7O4+(ZMn-6).*Mn6O4+(ZMn-3).*(Mn3+Mn3OH)...
   +(ZMn-2).*(Mn2+Mn2OH+Mn2SO4)+(ZC-4).*(H2CO3+HCO3+CO3)...
   +2.*(ZC-3).*(H2C2O4+HC2O4+C2O4)+(ZMn-3+2.*ZC-6).*Mn3C2O4...
   +(ZMn-3+4.*ZC-12).*Mn3C2O42+(ZMn-3+6.*ZC-18).*Mn3C2O43...
   +(ZMn-2+2.*ZC-6).*Mn2C2O4+(ZMn-2+4.*ZC-12).*Mn2C2O42+...
   +(ZMn-2+2.*ZC-6).*aa.*pr ...
   -((2.*ZC-6).*C0.*V0+(ZC-4).*C02.*V0+(ZC-4).*C1.*V...
   +(ZMn-7).*C.*V)./(V0+V))];

q=Mn2.*C2O4./Kso;

logMn2=log10(Mn2);
logMn2OH=log10(Mn2OH);
logMn2SO4=log10(Mn2SO4);
logq=log10(q);
logpr=log10(pr);
logMn2C2O4=log10(Mn2C2O4);
logMn2C2O42=log10(Mn2C2O42);
logMn3=log10(Mn3);
```

```
logMn3OH=log10(Mn3OH);
logMn3C2O4=log10(Mn3C2O4);
logMn3C2O42=log10(Mn3C2O42);
logMn3C2O43=log10(Mn3C2O43);
logMn6O4=log10(Mn6O4);
logMn7O4=log10(Mn7O4);
logH2CO3=log10(H2CO3);
logHCO3=log10(HCO3);
logCO3=log10(CO3);
logH2C2O4=log10(H2C2O4);
logHC2O4=log10(HC2O4);
logC2O4=log10(C2O4);
logHSO4=log10(HSO4);
logSO4=log10(SO4);
logNa=log10(Na);
logK=log10(K);
% The end of program
```