Comparative Balancing of Non-Redox and Redox Electrolytic Systems and Its Consequences

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ABSTRACT

In this paper, it is proved that linear combination $2\cdot f(O) - f(H)$ of elemental balances: $f(O)$ for O and $f(H)$ for H is linearly independent on charge and elemental/core balances for all redox systems of any degree of complexity; it is the primary form of the Generalized Electron Balance (GEB), $pr\text{-GEB} = 2\cdot f(O) - f(H)$, considered as the Approach II to GEB. The Approach II is equivalent to the Approach I based on the principle of common pool of electrons. Both Approaches are illustrated on an example of titration of acidified (H$_2$SO$_4$) solution of H$_2$C$_2$O$_4$ with KMnO$_4$. It is also stated, on an example of titration of the same solution with NaOH, that $2\cdot f(O) - f(H)$ is a linear combination of charge and elemental/core balances, i.e. it is not an independent balance when related to the non-redox system. These properties of $2\cdot f(O) - f(H)$ can be extended on redox and non-redox systems, of any degree of complexity, i.e. the linear independency/dependency of $2\cdot f(O) - f(H)$ on other balances related to a system in question is a criterion distinguishing redox and non-redox systems. The GEB completes the set of (charge and concentration) balances and a set of expressions for independent equilibrium constants needed for modeling the related redox system.

Keywords: Electrolytic Systems; Redox Systems; GEB; GATES

1. Introduction

Before 1992, the principle of formulation of a complete set of balances related to a redox system was unknown; except $k$ concentration balances and charge balance, the $k + 2$-th balance, completing the set of equations with $k + 2$ variables, was needed. All the trials [1-13] made after 1960s to find the missing equation were unsuccessful. Those trials were slavishly related to the stoichiometric reaction notations, involving only two pairs of species participating in redox reaction; the species different from those involved in the reaction notation were thus omitted in considerations. What is more, the charge balance and concentration balances for accompanying substances were also omitted. Theoretical considerations were related to virtual cases, not to real, electrolytic redox systems. In conclusion, all authors of those papers did not have any idea on how to resolve correctly the problem in question. The principle of the formulation of the $k + 2$-th equation, completing $k + 1$ equations composed of $k$ concentration balances and charge balance, was devised in 1992 by Michałowski in a totally mature form, known presently as the Approach I to Generalized Electron Balance (GEB). This Approach is based on a card game principle, with electron-active elements as “players”, electron-non-active elements as “fans”, and electrons as “money” (cash), constituting a common pool of electrons. The common pool of electrons is ascribed to players, whereas the fans’ cashes are untouched. The species in the related systems are considered in their natural form, i.e., as hydrates in aqueous media. For the species of $i$-th kind, $X_i^{z_i} \cdot n_i H_2O$, we apply the notation $X_i^{z_i} (N_i, n_i)$, where $n_i \geq 0$, $N_i$ is a number of these entities. The Approach I was formulated by Michałowski within the Generalized Approach to Electrolytic Systems (GATES). The GATES provides a comprehensive, compatible and consistent knowledge on thermodynamics of electrolytic redox and non-redox systems, referred to aqueous and non-aqueous media. The formulation of GATES, with GEB concept referred to redox systems, is denoted briefly as GATES/GEB. The first works on GATES, with the
The Approach I to GEB, presented first in [24] and then in other issues [25-30], is based on a linear combination $2\cdot f(O) - f(H)$ of the balances: $f(O)$ for oxygen (O) and $f(H)$ for hydrogen (H) related to redox systems; the balance $2\cdot f(O) - f(H)$ is considered as the primary form of GEB in redox systems $pr$-GEB = $2\cdot f(O) - f(H)$. The $pr$-GEB is linearly independent on charge and concentration balances in any electrolytic redox system (aqueous and non-aqueous media), whereas in any non-redox system the $2\cdot f(O) - f(H)$ is dependent on those balances. This property is thus the basis for a distinction between redox and non-redox electrolytic systems. The Approach II is fully equivalent to the Approach I to GEB.

The Approach II to GEB can be formulated for static (batch) and dynamic (titration) systems. In any titration, a titrant (T) is added into titrand (solution titrated, D) and a D + T system is thus formed. It is assumed that the D + T system and the subsystems (D and T) are closed (sub) systems, separated from the environment by diathermal walls; any flow of a matter between the environment and the system and its subsystems is not possible. The diathermal walls enable the related process ($T$—transposition sign)

$$\begin{align*}
a_1x_1 + a_2x_2 + \cdots + a_nx_n &= b_1 \\
a_1x_1 + a_2x_2 + \cdots + a_nx_n &= b_2 \\
\vdots \\
a_mx_1 + a_nx_2 + \cdots + a_nx_n &= b_m
\end{align*}$$

where $a_{ij}$ are numerical coefficients; some of the $a_{ij}$ values can be equal zero. To facilitate further reasoning, let us consider, for simplicity, the system of $m = 3$ equations with $n = 2$ variables, $x = [x_1, x_2]^T$, i.e.

$$\begin{align*}
a_{11}x_1 + a_{12}x_2 &= b_1 \\
a_{21}x_1 + a_{22}x_2 &= b_2 \\
a_{31}x_1 + a_{32}x_2 &= b_3
\end{align*}$$

where (1) and (2) are independent equations, i.e.

$$D = a_{11}a_{22} - a_{12}a_{21}$$

is $\neq 0$. For example, let us take the equations:

$$\begin{align*}
x_1 + x_2 &= 3 \quad (a_{11} = a_{12} = 1) \\
x_1 - x_2 &= 1 \quad (a_{21} = 1, \quad a_{22} = -1) \\
x_1 - 7x_2 &= -5 \quad (3a)
\end{align*}$$

On the basis of (1a), (2a), from (4) we get

$$D = 1\cdot(-1) - 1\cdot1 = -2 \neq 0,$$

and then $x_1 = 2, x_2 = 1$. Multiplication of (1a) by $-3$, (2a) by 4 and addition of the sides of the resulting equations gives (3a), i.e., (3a) is a linear combination of (1a) and (2a). Then (3a) is not an independent equation in this collection of equations, i.e., it depends linearly on (1a) and (2a).

In this paper, we apply more convenient (shorter) procedure to check the dependency of linear equations. This procedure is based on obtaining the identity, equivalent to the statement that $0 = 0$. For this purpose, we multiply (1a) by 3, (2a) by $-4$ and add the related sum to (3a)

$$\begin{align*}
3x_1 + 3x_2 &= 9 \\
-4x_1 + 4x_2 &= -4 \\
x_1 - 7x_2 &= -5
\end{align*}$$

Adding the Equations: (1b), (2b), (3b), we get the identity, $0 = 0$ (see also Appendix).

On this simple principle, we prove the linear de-
2.1. A Non-Redox System (System A)

V mL of T containing C mol/L NaOH + C₂ mol/L CO₂ is added into V₀ mL of D containing H₂C₂O₄ (C₀) + H₂SO₄ (C₀₁₁) + C₂O₂ mol/L CO₂. V₀ mL of D is composed of N₉₀ molecules of H₂C₂O₄·2H₂O + N₂₀₀ molecules of CO₂ + N₁₀₀ molecules of H₂SO₄ + Na₄₀ molecules of H₂O and V mL of T is composed of N₅₀ molecules of NaOH + N₆₀ molecules of CO₂ + N₇₀ molecules of H₂O. The following species:

H₂O (N₁); H⁺ (N₂, n₂), OH⁻ (N₃, n₃), HSO₄⁻ (N₄, n₄), SO₄²⁻ (N₅, n₅); Na⁺ (N₆, n₆), H₂C₂O₄ (N₇, n₇), HCO₃⁻ (N₈, n₈), C₂O₄²⁻ (N₉, n₉); H₂CO₃ (N₁₀, n₁₀), HCO₃⁻ (N₁₁, n₁₁), H₂C₂O₄ (N₁₂, n₁₂), CO₂⁻ (N₁₃, n₁₃), H₂SO₄ (N₁₄, n₁₄), MnO₄⁻ (N₁₅, n₁₅), Mn₃⁺ (N₁₆, n₁₆), MnO₂²⁻ (N₁₇, n₁₇), Mn₂⁺ (N₁₈, n₁₈), MnOH⁺ (N₁₉, n₁₉), MnSO₄ (N₂₁, n₂₁) are formed in the system in question. Note, for example, that N₁₀₀ molecules of H₂C₂O₄·2H₂O introduce 6N₁₀ electrons of H, 6N₁₀ atoms of O and 2N₁₀ atoms of C; N₆₀ ions of H₂SO₄·n₄H₂O contain N₄₀ (1 + n₄) atoms of H, N₆₀ (4 + n₄) atoms of O and 2N₆₀ atoms of C. On this basis, one can formulate the balances:

\[
\begin{align*}
  f(H) &= 2N₁ + N₂ (1 + 2n₂) + N₃ (1 + 2n₃) + N₄ (1 + 2n₄) \\
  & \quad + 2N₅₆₇₈ + 2N₆₇₈₉ + N₉ (2 + 2n₉) + N₁₀ (1 + 2n₁₀) \\
  & \quad + 2N₁₁₄₁₃ + N₁₂ (1 + 2n₁₂) + 2N₁₃₁₃ = 6N₁₀ + 2N₃₀ + 2N₄₀ + N₅₀ + 2N₇₀
\end{align*}
\]

\[
\begin{align*}
  f(O) &= N₁ + N₂n₂ + N₃ (1 + n₃) + N₄ (4 + n₄) + N₅ (4 + n₅) \\
  & \quad + N₆n₆ + N₇ (4 + n₇) + N₈ (4 + n₈) + N₉ (4 + n₉) \\
  & \quad + N₁₀ (3 + n₁₀) + N₁₁ (3 + n₁₁) + N₁₂ (3 + n₁₂) + N₁₃ (3 + n₁₃) \\
  & \quad = 6N₁₀ + 2N₁₅ + 4N₃₀ + 2N₄₀ + N₅₀ + 2N₆₀ + 2N₇₀
\end{align*}
\]

\[
\begin{align*}
  2f(O) - f(H) &= -N₂ + N₃ + 7N₄ + 8N₅ + 6N₆ + 7N₇ + 8N₈ + 4N₁₁ \\
  & \quad + 5N₁₂ + 6N₁₃ = 6N₁₀ + 2N₁₅ + 4N₃₀ + 2N₄₀ + N₅₀ + 2N₆₀ + 4N₇₀
\end{align*}
\]

Addition of (6) to charge balance (7), \(6f(Cₐₙ₅O₆)\) (8), \(6f(C₂O₄)\) (9), \(4f(CO₂)\) (10) and \(f(\text{Na})\) (11)

\[
\begin{align*}
  N₂ - N₃ - N₁₀ - 2N₄₅₆₇₈ + N₆₈ - N₈₉ - 2N₉₉ - N₁₂ - 2N₁₃ = 0
\end{align*}
\]

The term “core”, when referred to the species in electrolytic systems, means a common group of elements of the same composition and structure; e.g., C₄O₆ is a common core for different oxalate clusters: H₂C₂O₄, HCO₃⁻ and C₂O₄²⁻; SO₄ is a common core for different sulfate clusters: HSO₄⁻, SO₄²⁻ and MnSO₄.

2.2. A Redox System (System B)

V mL of T containing C mol/L KMnO₄ + C₂ mol/L CO₂ is added into V₀ mL of D containing H₂C₂O₄ (C₀) + H₂SO₄ (C₀₁₁) + C₂O₂ mol/L CO₂. V₀ mL of D is composed of N₉₀ molecules of H₂C₂O₄·2H₂O + N₂₀₀ molecules of CO₂ + N₁₀₀ molecules of H₂SO₄ and V mL of T is composed of N₅₀ molecules of KMnO₄ + N₆₀ molecules of CO₂ + N₇₀ molecules of H₂O. The following species:

H₂O (N₁); H⁺ (N₂, n₂), OH⁻ (N₃, n₃), HSO₄⁻ (N₄, n₄), SO₄²⁻ (N₅, n₅); K⁺ (N₆, n₆), H₂C₂O₄ (N₇, n₇), HCO₃⁻ (N₈, n₈), C₂O₄²⁻ (N₉, n₉); H₂CO₃ (N₁₀, n₁₀), HCO₃⁻ (N₁₁, n₁₁), H₂C₂O₄ (N₁₂, n₁₂), CO₂⁻ (N₁₃, n₁₃); MnO₄⁻ (N₁₄, n₁₄), Mn₃⁺ (N₁₅, n₁₅), Mn₂⁺ (N₁₆, n₁₆), MnOH⁺ (N₁₇, n₁₇), Mn²⁺ (N₁₈, n₁₈), MnOH⁺ (N₁₉, n₁₉), MnSO₄ (N₂₁, n₂₁) are formed in the system in question. Before addition of the first portion of the titrant (T), the solution is heated up to ca. 80°C; it is a metastable system at room temperature [26,28].

This system will be considered from the viewpoints of Approaches I and II to GEB. In the Approach I, Mn and C are considered as players whose electrons are balanced. The players are involved with fans in hydrates or other complexes.

2.2.1. Approach I to GEB

Denoting atomic numbers of Mn and C by Z₉₉ = 25 and Z₇₆ = 6, we state that N₉₀ molecules of KMnO₄ introduce \(N₉₀ = \{Z₉₉ - 7\} \) electrons, whereas the carbon components introduce \(2(Z₇₆ - 3)\) electrons to the common pool. In the resulting D + T system (solution), N₉₀ entities H₂C₂O₄·n₉H₂O involve (2Z₇₆-3) N₇₆ electrons, N₆₀ entities H₂C₂O₄·n₆H₂O involve 2 (Z₇₆-3) N₆₆ electrons... N₃₀ entities CO₂⁻·n₃H₂O involve (Z₇₆-4) N₃₀ electrons, N₂₁ entities MnO₄⁻·n₂₁H₂O involve (Z₇₆-7) N₂₁ electrons... N₂₁ entities MnSO₄·n₂₁H₂O involve (Z₇₆-2) N₂₁ electrons. Then the following balance is valid

\[
\begin{align*}
  2(Z₇₆ - 3)(N₇₆ + N₆₈ + N₅₉) + (Z₇₆ - 4)(N₁₅ + N₁₂ + N₁₃) \\
  + (Z₇₆ - 7)N₂₁ + (Z₇₆ - 6)N₁₅ + (Z₇₆ - 3)(N₁₁ + N₁₇) \\
  + (Z₇₆ - 2)(N₁₈ + N₁₉ + N₂₁) = 2(Z₇₆ - 3)N₆₀ + 2(Z₇₆ - 3)N₃₀ + (Z₇₆ - 7)N₂₁
\end{align*}
\]

Applying the relations:
We formulate the balances:

\[
\left[ X^{n+} \right] (V_0 + V) = 10^3 \cdot N_i / N_A, \quad C_0 V_0 = 10^3 \cdot N_{10} / N_A, \\
CV = 10^3 \cdot N_{50} / N_A, \quad C_{01} V_0 = 10^3 \cdot N_{20} / N_A, \\
C_i V = 10^3 \cdot N_{60} / N_A 
\]

(13)

in (12), we get the equation

\[
2(Z_c - 3) \left[ \left[ H_2C_2O_4^+ \right] + \left[ HC_2O_4^- \right] + \left[ C_2O_4^{2-} \right] \right] \\
+ (Z_c - 4) \left[ \left[ H_2CO_3 \right] + \left[ HCO_3^- \right] + \left[ CO_3^{2-} \right] \right] \\
+ (Z_{Mn} - 7) \left[ \left[ MnO_4^- \right] + (Z_{Mn} - 6) \left[ MnO_4^{2-} \right] \right] \\
+ (Z_{Mn} - 3) \left[ \left[ MnO_3^{3-} \right] + \left[ MnOH^{2+} \right] \right] \\
+ (Z_{Mn} - 2) \left[ \left[ MnO_2^- \right] + \left[ MnOH^- \right] + \left[ MnSO_4^{2-} \right] \right] \\
= \left( (Z_c - 3) CV \right) / (V_0 + V) 
\]

(14)

2.2.2. Approach II to GEB

We formulate the balances:

\[
f(H) \\
2N_i + N_2 \left( 1 + 2n_2 \right) + N_3 \left( 1 + 2n_3 \right) + N_4 \left( 1 + 2n_4 \right) \\
+ 2N_i n_4 + 2N_2 n_2 + 2N_3 n_3 + N_2 \left( 2 + n_2 \right) + N_3 \left( 2 + n_3 \right) \\
+ 2N_4 n_2 + N_1 n_1 \left( 2 + n_1 \right) + N_2 \left( 1 + n_2 \right) + 2N_3 n_1 \\
+ 2N_4 n_3 + 2N_1 n_1 + 2N_3 n_2 + 2N_4 n_1 + N_4 \left( 1 + n_4 \right) + 2N_4 n_4 \\
+ N_1 \left( 1 + 2n_1 \right) + 2N_2 n_1 = 6N_{10} + 2N_{30} + 2N_{40} + 2N_{50} 
\]

(15)

\[
f(O) \\
N_i + N_2 n_2 + N_3 \left( 1 + n_3 \right) + N_4 \left( 1 + n_4 \right) + N_5 \left( 4 + n_5 \right) \\
+ N_5 n_5 + N_1 \left( 4 + n_4 \right) + N_2 \left( 4 + n_2 \right) + N_2 \left( 4 + n_2 \right) \\
+ N_1 \left( 3 + n_1 \right) + N_2 \left( 3 + n_2 \right) + N_3 \left( 3 + n_3 \right) \\
+ N_4 \left( 4 + n_4 \right) + N_5 \left( 4 + n_5 \right) + N_6 \left( 4 + n_6 \right) + N_7 \left( 1 + n_7 \right) \\
+ N_8 n_8 + N_9 \left( 1 + n_9 \right) + N_{10} \left( 4 + n_{10} \right) \\
= 6N_{10} + 2N_{30} + 4N_{30} + 4N_{40} + 4N_{50} + 2N_{60} + N_{70} 
\]

(16)

\[
2f(O) - f(H) = pr-GEW \\
- N_2 + N_3 + 7N_4 + 8N_5 + 6N_7 + 7N_6 + 8N_9 + 4N_{11} \\
+ 5N_{12} + 6N_{13} + 8N_{14} + 8N_{15} + N_{17} + N_{19} + 8N_{21} \\
= 6N_{10} + 4N_{20} + 6N_{30} + 8N_{50} + 4N_{60} 
\]

(17)

Addition of (17) to charge balance (18), 6f(SO4) (19) and f(K) (20)

\[
N_2 - N_3 - N_4 - 2N_5 + N_6 - N_8 - 2N_9 - N_{12} - 2N_{13} \\
- N_{14} - 2N_{15} + 3N_{16} + 2N_{17} + 2N_{18} + N_{19} = 0 \\
6N_{50} = 6N_4 + 6N_5 + 6N_{21} 
\]

(18) (19)

\[
N_{50} = N_6 
\]

(20)

Introducing the relations (13) to (22), we get the equation identical with (14); it proves the equivalency of the Approaches I and II to GEB. Equation (14) is considered as GEB for the related system. However, the equation

\[
- \left[ H^+ \right] + \left[ OH^- \right] + 7 \left[ HSO_4^- \right] + 8 \left[ SO_4^{2-} \right] + 6 \left[ H_2C_2O_4^- \right] \\
+ 7 \left[ HC_2O_4^- \right] + 8 \left[ C_2O_4^{2-} \right] + 4 \left[ H_2CO_3 \right] + 5 \left[ HCO_3^- \right] \\
+ 6 \left[ CO_3^{2-} \right] + 8 \left[ MnO_4^- \right] + 8 \left[ MnO_4^{2-} \right] + \left[ MnOH^{2+} \right] + \left[ MnOH^- \right] + 8 \left[ MnSO_4^{2-} \right] \\
= \left( 6C_0 V_0 + 4 \left( C_{02} V_0 + C_2 V \right) \right) / (V_0 + V) + 6C_{01} V_0 + 8CV 
\]

(21)

obtained after application of the relations (13) and \( C_{01} V_0 = 10^3 \cdot N_{50} / N_A \) in (17) and any other combination of (17) with other (charge and/or elemental/core) balances provides an equivalent form of GEB. For example, subtraction of \( (Z_c - 4) f(C) + (Z_{Mn} - 2) f(Mn) \) from (12) and application of (13) gives the simplest (in terms of the number of components) form of GEB

\[
2 \left[ H_2C_2O_4^- \right] + \left[ HC_2O_4^- \right] + \left[ C_2O_4^{2-} \right] \\
- 5 \left[ MnO_4^- \right] - 4 \left[ MnO_4^{2-} \right] + \left[ MnO_3^{3-} \right] + \left[ MnOH^{2+} \right] \\
= \left( 2C_0 V_0 - 5CV \right) / (V_0 + V) 
\]

(22)

which is one of the equivalent forms of GEB, referring to the system in question. As we see, application to the redox system of the same procedure, i.e., linear combination of the corresponding set of equations, does not lead to the identity, but a new balance, independent from charge and concentration balances, is obtained.
3. Completing the Set of Balances

The GEB, expressed e.g. by Equation (24), is completed by charge (see Equation (18))

\[
\begin{align*}
[\text{H}^+] & - [\text{OH}^-] - [\text{HSO}_4^-] - 2[\text{SO}_4^{2-}] + [\text{K}^+] \\
- [\text{HC}_2\text{O}_4^-] & - 2[\text{C}_2\text{O}_4^{2-}] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] \\
- [\text{MnO}_4^-] & - 2[\text{MnO}_2^{2-}] + 3[\text{Mn}^{3+}] + 2[\text{MnOH}^{2+}] \\
+ 2[\text{Mn}^{2+}] + [\text{MnOH}^+] & = 0
\end{align*}
\]

and concentration balances:

\[
\begin{align*}
\text{j(C)} & = 2[\text{H}_2\text{C}_2\text{O}_4^-] + 2[\text{HC}_2\text{O}_4^-] + 2[\text{C}_2\text{O}_4^{2-}] + [\text{H}_2\text{CO}_3^-] \\
& + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = (2\text{C}_0\text{V}_0 + \text{C}_{\text{Mn}}\text{V}_0 + \text{C}_2\text{V}_0)/(\text{V}_0 + \text{V}) \\
\text{j(Mn)} & = [\text{MnO}_4^-] + [\text{MnO}_2^{2-}] + [\text{Mn}^{3+}] + [\text{MnOH}^{2+}] + [\text{Mn}^{2+}] \\
& + [\text{MnOH}^+] + [\text{MnSO}_4^-] = \text{CV}/(\text{V}_0 + \text{V}) \\
\text{j(S)} \text{ or } \text{j(SO}_4^-) & = [\text{HSO}_4^-] + [\text{SO}_4^{2-}] + [\text{MnSO}_4^-] = \text{C}_0\text{V}_0/(\text{V}_0 + \text{V})
\end{align*}
\]

The relation \( K^+ = CV/(V_0 + V) \) (see Equation (20)) is not considered as a concentration balance; at defined \( C \), \( V \), \( V_0 \) values, it enters as a number in the charge balance (25).

It should be noticed that the species with different cores, namely \( \text{C}_2\text{O}_4^- \) and \( \text{CO}_3^{2-} \), are involved in the same balance (26). It results from the fact that oxalate species are transformed in the System B into carbonate species, i.e., a change in the core occurs. Such a transformation does not occur in the System A, where the balances for oxalates and carbonates can be written as separate equations.

4. Completing the Set of Equilibrium Constants

The set of (GEB, charge and concentration) balances is completed by interrelations between concentrations of the species entering these balances. These interrelations are expressed by a set of expressions for independent equilibrium constants. These equilibrium constants, obtained from tables of equilibrium constants [37-39] values, are involved with non-redox:

\[
\begin{align*}
\text{H}_2\text{O} &= \text{H}^+ + \text{OH}^- \quad (\text{pK}_w = 14), \quad [\text{OH}^-] = 10^{\text{pK}_w - 14} \\
\text{H}_2\text{C}_2\text{O}_4^- &= \text{H}^+ + \text{HC}_2\text{O}_4^- \quad (\text{pK}_a = 1.25) \\
[\text{HC}_2\text{O}_4^-] &= 10^{\text{pK}_a - 1.25} \cdot [\text{H}_2\text{C}_2\text{O}_4^-] \\
\text{HC}_2\text{O}_4^- &= \text{H}^+ + \text{C}_2\text{O}_4^{2-} \quad (\text{pK}_a = 4.27) \\
[\text{C}_2\text{O}_4^{2-}] &= 10^{\text{pK}_a - 4.27} \cdot \text{[H}_2\text{C}_2\text{O}_4^-] \\
\text{H}_2\text{CO}_3^- &= \text{H}^+ + \text{HCO}_3^- \quad (\text{pK}_a = 6.3) \\
[\text{HCO}_3^-] &= 10^{\text{pK}_a - 6.3} \cdot \text{[H}_2\text{CO}_3^-] \\
\text{HCO}_3^- &= \text{H}^+ + \text{CO}_3^{2-} \quad (\text{pK}_a = 10.1) \\
[\text{CO}_3^{2-}] &= 10^{\text{pK}_a - 10.1} \cdot \text{[HCO}_3^-] \\
\text{HSO}_4^- &= \text{H}^+ + \text{SO}_4^{2-} \quad (\text{pK}_a = 1.8) \\
[\text{SO}_4^{2-}] &= 10^{\text{pK}_a - 1.8} \cdot \text{[HSO}_4^-] \\
\text{Mn}^{3+} + \text{OH}^- &= \text{MnOH}^{2+} \quad (\text{log } \text{K}_{\text{OH}}^+ = 14.2) \\
[\text{MnOH}^{2+}] &= 10^{\text{pK}_a - 0.2} \cdot \text{[Mn}^{3+}] \\
\text{Mn}^{2+} + \text{OH}^- &= \text{MnOH}^+ \quad (\text{log } \text{K}_{\text{OH}}^+ = 3.4) \\
[\text{MnOH}^+] &= 10^{\text{pK}_a - 10.6} \cdot \text{[Mn}^{2+}] \\
\text{Mn}^{2+} + \text{SO}_4^{2-} &= \text{MnSO}_4^- \quad (\text{log } \text{K}_f = 2.28) \\
[\text{MnSO}_4^-] &= 10^{2.28} \cdot \text{[Mn}^{2+}] \cdot \text{[SO}_4^{2-}] \\
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- &= \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad (E_0 = 1.507 \text{ V}) \\
[\text{MnO}_4^-] &= [\text{Mn}^{2+}] \cdot 10^{5.4 \cdot (E - 1.507) - 8 \cdot \text{pH}} \\
\text{MnO}_4^- + \text{e}^- &= \text{MnO}_4^- \quad (E_0 = 0.56 \text{ V}) \\
[\text{MnO}_4^-] &= [\text{MnO}_4^-] \cdot 10^{-4 \cdot (E - 0.56)} \\
\text{Mn}^{3+} + \text{e}^- &= \text{Mn}^{2+} \quad (E_0 = 1.509 \text{ V}) \\
[\text{Mn}^{3+}] &= [\text{Mn}^{2+}] \cdot 10^{-4 \cdot (E - 1.509)} \\
2\text{H}_2\text{CO}_3^- + 2\text{H}^+ + 2\text{e}^- &= \text{H}_2\text{C}_2\text{O}_4^- + 2\text{H}_2\text{O} \quad (E_0 = -0.386) \\
[\text{H}_2\text{C}_2\text{O}_4^-] &= [\text{H}_2\text{C}_2\text{O}_4^-] \cdot 10^{(E_0 + 0.386) - \text{pH}}
\end{align*}
\]

where: \( \text{pH} = -\log[\text{H}^+] \), \( A = F/(RT \cdot \ln 10) \), \( F = \text{Faraday constant, } R = \text{gas constant, } T = \text{temperature (K), } A = 16.92 \text{ at } 298 \text{ K. All attainable (qualitative and quantitative) knowledge is involved in these balances and equilibrium constants. Other species, e.g. Mn(SO}_4)_{3-2j} \text{ complexes, are unknown in literature, see 17,28. The requirement involved with independent set of equilibrium constants prevents receiving of contradictory equations.} \)

It is assumed that the solution in the redox system is sufficiently acidified (\( \text{H}_2\text{SO}_4 \)) 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 (27).
5. Prevention of Contradictory Equations

As were stated above, GEB is fully compatible with charge and concentration balances. The balances should be arranged rightly; it means that all known species from the system in question should be included properly and consequently in the related balances. All more complex species should be involved in expressions for the related equilibrium constants.

Tables of the equilibrium constants usually contain redundant and incompatible equilibrium constants values. The equilibrium constants were determined experimentally, then the quoted values of a defined equilibrium constant may be different in different tables. For example, the pH value found in for acetic acid is 4.65 [37] (at 1 = 0.1 mol/L, without indication of temperature) and 4.76 [38] (at 25°C, without indication of ionic strength, I). However, some hidden divergence in the equilibrium data is usually encountered in the same book. For example, the pK1 value found in [38] for the system in question should be included properly and consequently in the related balances. All more complex species should be involved in expressions for the related equilibrium constants.

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The properties of 2f(O) − f(H) of elemental balances: f(H) for H and f(O) for O were referred to non-redox and redox systems (aqueous media), denoted as System A and System B, respectively. It was assumed that the composition of titrant (D) is the same, but the titrants applied were different: NaOH in the System A, and KMnO4 in the System B.

In the System A (non-redox system), it was stated that 2f(O) − f(H) is the linear combination of charge and other elemental or core balances: f(Na), f(SO3), f(C2O4), and f(CO3), i.e. 2f(O) − f(H) are not independent balances in this system.

In the System B (redox system) 2f(O) − f(H) is independent on those balances. For redox systems, 2f(O) − f(H) is the primary form of Generalized Electron Balance (GEB), obtained according to Approach II.

These properties are valid for non-redox and redox systems of any degree of complexity. The linear dependency/independency property of 2f(O) − f(H) is then a new criterion distinguishing non-redox and redox systems.

The Approach II is equivalent to the Approach I; the latter is based on the common pool of the electron principle. However, the Approach II offers special advantages, of capital importance, particularly when referred to redox systems, where complex organic species are considered. Namely, the knowledge of oxidation numbers of all elements and structure of the elements in these species is not needed. A known composition of all the species, expressed by their formula and external charge, provides information sufficient to formulate the related GEB. In particular, the Approach II is convenient in formulation of GEB for the systems where radicals and ion-radicals are formed. The Approach I to GEB, considered as a “short” version of GEB, is applicable for the systems where oxidation degree can easily be calculated for all elements in the redox system in question.

The properties of 2f(O) − f(H) can be extended on non-redox or redox systems of any degree of complexity. These properties can also be extended on mixed-solvent systems, where polar protic (e.g. H2O, CH3OH) or aprotic (e.g. (CH3)2SO) solvents are involved.

The terms: “oxidant” and “reductant” are not necessary (not applicable) in considerations on a redox system [24-28]. Different species are considered in their natural form, i.e. as solvates, e.g. hydrates in aqueous media; although the systems with mixed solvents (e.g. binary-solvent systems) were also considered [40].

The Approach II shows that GEB is based on reliable principles of the matter conservation, and—in this regard—it is equally robust as equations for charge and concentration balances. From this viewpoint, GEB is considered as a relatively new law of Nature, referring to electrolytic redox systems of any degree of complexity, namely equilibrium, metastable, non-equilibrium, mono- and poly-phase systems [28].

GEB completes the set of charge and concentration balances and a complete set of independent expressions for equilibrium constants, needed for quantitative description of redox system.

In summary, GEB, charge and concentration balances, together with the set of independent equilibrium constants, provide the numerical algorithm, implemented to software packages that support advanced programming, such as MATLAB computing environment. The calculation procedure, based on iterative computer programs [28], enables the desired relationships to be plotted graphically.

REFERENCES


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Appendix (a More Sophisticated Presentation of the Linear Dependency)

Let us take the set of linear equations:

\[
\begin{align*}
a_1 x_1 + a_2 x_2 + a_3 x_3 &= b_1 \\
a_2 x_1 + a_2 x_2 + a_3 x_3 &= b_2
\end{align*}
\]

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

\[
c_1 (a_1 x_1 + a_2 x_2 + a_3 x_3) + c_2 (a_1 x_1 + a_2 x_2 + a_3 x_3) = (c_1 a_1 + c_2 a_2) x_1 + (c_1 a_1 + c_2 a_2) x_2 + (c_1 a_3 + c_2 a_3) x_3 = c_1 b_1 + c_2 b_2.
\]

Applying matrix algebra we see that the determinant

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

has zero value

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

irrespectively on the \(c_1\) and \(c_2\) values; at \(D = 0\), calculation of \(x_1\), \(x_2\) and \(x_3\) is impossible. On the other hand, even a small change in the third equation makes a system of equations contradictory. For example, taking the system of equations: (1a), (2a) (see text) and (α) \(x_1 - 7x_2 = -5.01\), (β) \(1.01x_1 - 7x_2 = -5\), (γ) \(x_1 - 7.01x_2 = -5\) instead of (3a) we get the contradictions: \(-5 \neq -5.01\) in (α) and (γ), and \(-4.98 \neq -5\) in (β).