General Properties of the Balance $2f(O) - f(H)$ in Electrolytic systems. Some Detailed Remarks on Elemental versus Core Balances

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Abstract

Any electrolytic system in aqueous media is described with use of charge balance, $f_0 = ChB$, and K elemental or core balances, $f_k = f(Y_k)$ ($k = 1,...,K$). The balances: $f_1 = f(H)$ and $f_2 = f(O)$ are the basis to formulate the linear combination $f_{12} = 2f_1 - f_2 = 2f(O) - f(H)$. For a redox system with K–K electron-active elements (players), $f_{12}$ is linearly independent on $f_0, f_{12}, f_{2}$, i.e., the redox system is described by K independent balances $f_1, f_2, f_{12}, f_k$ for a non-redox system (K-K), $f_{12}$ is linearly dependent on $f_0, f_{12}, f_k$ i.e., $f_{12}$ is the primary form of Generalized Electron Balance (GEB). The paper is completed by description of typical redox and non-redox systems according to GATES/GEB principles.

Keywords: Electrolytic redox systems, GATES/GEB, Approach I to GEB, Approach II to GEB, Potentiometric titration.

Introduction

The article concerns fundamental regularities, obligatory for electrolytic systems of different complexity, considered from the viewpoint of Generalized Approach to Electrolytic Systems (GATES), formulated by Michałowski (1992) [1,2]. According to GATES, a balancing of any electrolytic system is based on rules of conservation of particular elements, and on a charge balance, expressing the rule of electro-neutrality of this system. We refer to aqueous media, $W=H_2O$, where the species $X^{±}_{zi}, n_{zi}, x_i = 0, ± 1, ± 2,...$ is a charge, expressed in elementary charge units, $e = F/N_A$ ($F$ = Faraday’s constant, $N_A$ = Avogadro’s number, $n_i = n_{zi} = n_{h2o}$ molecule attached to $X^{±}_{zi}$. For ordering purposes, we assume $Y_1 = H$ (hydrogen) and $Y_2 = O$ (oxygen), and formulate first the linear combination

$$f_{12} = 2f_2 - f_1 = 2f(O) - f(H)$$

of elemental balances: $f_1 = f(H)$ for hydrogen (H) and $f_2 = f(O)$ for oxygen (O), related to the system considered. Then the linear combination of $f_{12}$ with charge balance ($f_0$) and elemental/core balances $f_k = f(Y_k)$ ($k=3,...,K$) for elements/cores $Y_k ≠ H, O$ will be formulated [3]. A core is considered as a cluster of different atoms with defined composition (expressed by chemical formula), structure and external charge, e.g. $SO_3^{2-}$ is a core with external charge $-2$, composed of two elements: S and O. The balances $f_k (k=1,...,K)$ interrelate the numbers of different elements...
cores in components forming a system, and in the species thus formed. The notation of the balances \( f_{ij} \) relates the balance here as is follows

\[
f_i = \{ c_{ik} \} - \{ s_{ik} \} = 0 \iff -f_i = \{ c_{ik} \} - \{ s_{ik} \} = 0 \iff -f_i : \{ c_{ik} \} \iff -f_i : \{ s_{ik} \}
\]

where \( c_{ik} \) is referred to a set of some components, \( \{ c_{ij} \} \) to some species in \( k \)-th balance; \( c_{0k} = 0 \), i.e., \( c_{0k} = \phi \) (empty set, for \( f \)). Numbers of components of \( j \)-th kind are denoted by \( N_{0j} \), numbers of the species \( s_{ik} \) of \( i \)-th kind are denoted by \( N_i \).

For balancing purposes, the hydrated species \( X_{z,j}^{\pm} n_m \) in the system are specified as \( X_{z,j}^{\pm} (N_j, n) \); e.g., the notation HSO\(_4\) applied in Example 1 below refers to \( N_i \) ions of HSO\(_4\) in \( n \) involving: \( N_i (1+2n) \) atoms of \( H \), \( N_i (4+n) \) atoms of \( O \), and \( N_i \) atoms of S. Molar concentration of the species \( X_{z,j}^{\pm} n_m \) be denoted by \( X_{z,j}^{\pm} \).

The \( f_{ij} \) (Equation 1) is the primary form of Generalized Electron Balance (GEB), \( f_{ij} = pr-\text{GEB} \) formulated (2005) for redox systems according to Approach II to GEB, where prior knowledge of ONs of all elements in components and species is not needed. The Approach II to GEB is fully compatible with the Approach I to GEB [4-15] formulated (1992) and based on the principle of common pool of electrons involved in non-redox system, e.g., 'players' and distinguished from electron-non-active elements considered as 'fans', when a redox system is considered according to card game principle [15]: ONs for elements in components and species are needed in the Approach I. The principles of GEB formulation, discovered (1992, 2005) by Michałowski and resolved according to Generalized Approach to Electrolytic Systems (GATES) as GATES/GEB [1,16], were unknown in earlier literature.

GEB completes the set of K balances \( f_{ij} \) as algebraic equations necessary for solving a redox system; K-1 balances \( f_{ij} \) are required for solving a non-redox system; \( f_{ij} \) is omitted as derivative (not primary) balance. GEB is the law of Nature related to equilibrium, metastable complexes in components forming a system, and in the species thus formed. The notation of the balances \( f_{ij} \) applied non-redox systems of different degree of complexity. For a non-redox system

\[
f_{ij} + f_0 - \sum_{i=0}^{K} d_i f_i = 0 \iff \sum_{i=0}^{K} d_i \cdot f_i - f_0 = 0
\]

is transformed into identity, \( 0 = 0 \). We prove that the equation (3)

\[
(1^o) \text{ implies a general criterion distinguishing between non-redox and redox systems;}
(2^o) \text{ defines } \delta_i \text{ as oxidation numbers (ONs) of particular elements in components and species of a non-redox or redox system.}
\]

Synthesis of chemical and physical laws of conservation is expressed, respectively, by the equalities of left and right sides of Equations (3) and (3a).

**Formulation of Non-Redox Systems**

**Example 1:** The (static) system is formed from the following components: Na\(_2\)S\(_9\)H\(_4\)O \((N_{09})\), Na\(_2\)SO\(_4\) \((N_{011})\) (Sal Mirabilis), H\(_2\)O \((N_{03})\). The species in the system thus formed, namely:

\[
\begin{align*}
H_2O (N_0), H^+ & (N_{01}), OH^- & (N_1), Na^+ & (N_{02}), HSO_4^- & (N_{05}), SO_4^{2-} & (N_{06}), H^+ & (N_{01}), H^- & (N_1), Na^+ & (N_{02}),
\end{align*}
\]

are involved in the following balances:

\[
f_0 = \text{ChB}:
N_2 - N_4 + N_5 - N_6 - 2N_8 - 2N_9 = 0
f_1 = f(H):
2N_{1_0} + N_6(1+2n) + N_5(1+2n) + 2N_4n_9 + N_5(1+2n) + 2N_4n_9
+ N_5(2+2n) + N_5(1+2n) + 2N_4n_9
= 18N_{01} + 20N_{02} + 2N_{03}
\]

\[
f_2 = f(Na):
N_1 + N_2n_9 + N_4(1+n) + N_5n_9 + N_4(4+n) + N_5n_9 + N_5n_9 + N_5n_9 = 9N_{01} + 14N_{02} + N_{03}
\]

\[
f_{ij} = 2f_2 - f_1:
N_2 + N_3 + 7N_5 + 8N_6 - 2N_7 - N_8 = 8N_{02}
-f_3 = -f(Na):
2N_{01} + 2N_{02} = N_9
-6f_4 = 6f(SO_4):
6N_{02} - 6N_5 + 6N_6
2f_5 = 2f(S):
N_2 + 2N_{01} + 2N_{02} = 2N_{01}
f_{ij} + f_0 - f_3 - 6f_4 + 2f_5
= 0
\]

i.e., the linear combination (4) is transformed into identity; it can be rewritten into the form

\[
(1^o)f_1 + (-2)f_2 + (1)f_3 + (6)f_4 + (-2)f_5 = 0 \quad \Rightarrow
(1^o)f(H) + (-2)f(O) + (1)f(Na)
+ (6)f(SO_4) + (-2)f(S) - \text{ChB} = 0
\]

where the numbers in round brackets as multipliers for \( f \) are equal to ONs of the related elements. Within \( f_{ij} \) and then within (5), \( N_0 \) and all \( n_i \) values, within components and species, are cancelled. The species \( X_{z,j}^{\pm} n_m \) not involving
H and/or O within $\chi^i$, are also cancelled within $f_{i2}$. More specifically, the $f_i$ involving only one kind of species, is considered here as equality, not as equation.

In this system, symproporation [21] of sulfur does not occur; from this viewpoint, the system is at a metastable state [1,13]. Consequently, all elements (H, O, Na, S) involved in this system are perceived as fans, i.e., $K' = K = 4$. Sulfide oxidation can occur in presence of sulfate-reducing bacteria [34]. Sulfide gives sulfate after oxidation with $\text{H}_2\text{O}_2$ [35], whereas sulfate ions are not reducible in usual procedure [36].

The elemental balance for $\text{S}$ is $f(S) = f_i = f_1 + f_2$.

The linear combination $f_{i2} = 0 = f_2 + p_1 f_1$, $f_{i3}$, $f_{i4}$ is not transformable into identity 0 = 0, at any p-value. From (6) and (4) we get the contradiction $p = 6$ and $p = -2$, i.e., $f_{i1}$ is not applicable for checking $f_1$ (Eq. 1) as the criterion of independency of the related balances.

Example 2 (dynamic system). $V_0$ mL of titrand (D), containing $\text{ZnSO}_4\cdot \text{H}_2\text{O}$ (goslarite), $N_{02}$ molecules of $\text{NH}_3$, $N_{03}$ molecules of $\text{H}_2\text{O}$, $N_{10}$ molecules of $\text{NaH}_2\text{O}$, $N_{11}$ molecules of $\text{NaH}_2\text{O}_2$, $N_{20}$ molecules of $\text{H}_2\text{O}$, $N_{13}$ molecules of $\text{EDTA}$ (erio T, $C_{16}$) is titrated with $V$ mL of titrant (T) containing EDTA (C) [3].

The D is composed of $N_{01}$ molecules of $\text{ZnSO}_4\cdot \text{H}_2\text{O}$ (goslarite), $N_{02}$ molecules of $\text{NH}_3$, $N_{03}$ molecules of $\text{H}_2\text{O}$, $N_{10}$ molecules of $\text{NaH}_2\text{O}$, $N_{11}$ molecules of $\text{NaH}_2\text{O}_2$ of $\text{H}_2\text{O}$, $N_{13}$ molecules of $\text{EDTA}$ (erio T, $C_{16}$) is titrated with $V$ mL of titrant (T) containing EDTA (C) [3].

The D is composed of $N_{01}$ molecules of $\text{ZnSO}_4\cdot \text{H}_2\text{O}$ (goslarite), $N_{02}$ molecules of $\text{NH}_3$, $N_{03}$ molecules of $\text{H}_2\text{O}$, $N_{10}$ molecules of $\text{NaH}_2\text{O}$, $N_{11}$ molecules of $\text{NaH}_2\text{O}_2$, $N_{13}$ molecules of $\text{EDTA}$ (erio T, $C_{16}$) is titrated with $V$ mL of titrant (T) containing EDTA (C) [3].

The D is composed of $N_{01}$ molecules of $\text{ZnSO}_4\cdot \text{H}_2\text{O}$ (goslarite), $N_{02}$ molecules of $\text{NH}_3$, $N_{03}$ molecules of $\text{H}_2\text{O}$, $N_{10}$ molecules of $\text{NaH}_2\text{O}$, $N_{11}$ molecules of $\text{NaH}_2\text{O}_2$, $N_{13}$ molecules of $\text{EDTA}$ (erio T, $C_{16}$) is titrated with $V$ mL of titrant (T) containing EDTA (C) [3].

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The D is composed of $N_{01}$ molecules of $\text{ZnSO}_4\cdot \text{H}_2\text{O}$ (goslarite), $N_{02}$ molecules of $\text{NH}_3$, $N_{03}$ molecules of $\text{H}_2\text{O}$, $N_{10}$ molecules of $\text{NaH}_2\text{O}$, $N_{11}$ molecules of $\text{NaH}_2\text{O}_2$, $N_{13}$ molecules of $\text{EDTA}$ (erio T, $C_{16}$) is titrated with $V$ mL of titrant (T) containing EDTA (C) [3].

The D is composed of $N_{01}$ molecules of $\text{ZnSO}_4\cdot \text{H}_2\text{O}$ (goslarite), $N_{02}$ molecules of $\text{NH}_3$, $N_{03}$ molecules of $\text{H}_2\text{O}$, $N_{10}$ molecules of $\text{NaH}_2\text{O}$, $N_{11}$ molecules of $\text{NaH}_2\text{O}_2$, $N_{13}$ molecules of $\text{EDTA}$ (erio T, $C_{16}$) is titrated with $V$ mL of titrant (T) containing EDTA (C) [3].
The formula $C\text{}_\text{20}H\text{}_{114}N\text{}_8O\text{}_7$ for the neutral species of erio T can be rewritten into the form $(C\text{}_{20}N\text{}_8S)(H\text{}_2O)\text{OH}$. The group of elements within $C\text{}_{20}N\text{}_8S$ has the net charge $x$ calculated from the equation $1\times 6\times (0) + 1\times (2+1) = 0 \Rightarrow x=1$. Similarly, in $C\text{}_5H\text{}_8N\text{}_9O\text{}_4 = (C\text{}_5N\text{}_9S)(H\text{}_2O)\text{OH}$, the net charge $x$ of the $C\text{}_5N\text{}_9S$ group is calculated from the equation $1\times 8\times 0 = 0$, i.e., $x = 0$. The $C\text{}_5N\text{}_9S$ and $C\text{}_5N\text{}_9$ can be also (optionally) considered as cores.

The $f_0, f_2, f_4, f_6, f_8$ are specified separately, for different cores: $SO_4^{2–}, NH\text{}_4$, $C_5H\text{}_8N\text{}_9O\text{}_4$, $C\text{}_5H\text{}_8N\text{}_9O\text{}_4$, respectively. Note that S enters the compounds and species in $f_0, f_2, f_4$; N enters the compounds and species in $f_6, f_8$. Furthermore, none transgressions occur between the cores of the species belonging to separate concentration balances.

Referring again to the species involved with erio T, one can write the elemental balances: $N\text{}_{21} + N\text{}_{22} + N\text{}_{23} + N\text{}_{24} + N\text{}_{25} + 2N\text{}_{26} = N\text{}_{34}$ (for S); $3N\text{}_{21} + 3N\text{}_{22} + 3N\text{}_{23} + 3N\text{}_{24} + 3N\text{}_{25} + 6N\text{}_{26} = 3N\text{}_{34}$ (for N); $20N\text{}_{21} + 20N\text{}_{22} + 20N\text{}_{23} + 20N\text{}_{24} + 20N\text{}_{25} + 40N\text{}_{26} = 20N\text{}_{34}$ (for C).

All the equations are identical and equivalent to Eq. (8), because the core $C\text{}_5H\text{}_{10}N\text{}_2O\text{}_2S$ is unchanged in reactions occurring during the titration. Similarly, the species involved with EDTA fulfill the relations: $10N\text{}_{27} + 10N\text{}_{28} + 10N\text{}_{29} + 10N\text{}_{30} + 10N\text{}_{31} + 10N\text{}_{32} + 10N\text{}_{33} + 10N\text{}_{34} + 10N\text{}_{35} + 10N\text{}_{36} = 10N\text{}_{36}$ (for C), and $3N\text{}_{27} + 3N\text{}_{28} + 3N\text{}_{29} + 3N\text{}_{30} + 3N\text{}_{31} + 3N\text{}_{32} + 3N\text{}_{33} + 3N\text{}_{34} + 3N\text{}_{35} + 3N\text{}_{36} = 3N\text{}_{36}$ (for N). Both equations are equivalent to $f_0$ Eq. (9).

Denoting the elemental balances for S, N and C as $f(S) = f_{68}$, $f(N) = f_{78}$, $f(C) = f_{88}$, we have the relations, expressed in the matrix form as follows

$$
\begin{bmatrix}
78 & 0 & 0 \\
68 & 1 & 0 \\
88 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
 f_6 \\
 f_7 \\
 f_8
\end{bmatrix}
= 0
$$

One can prove that the linear combination

$$
\begin{align*}
f_6 + f_7 + f_8 + p f_{68} + q f_{78} + r f_{88}
\end{align*}
$$

is not transformable into identity $0 = 0$, at any of the (p, q, r) values. Namely, from Equations (10) and (12) we get

$$
\begin{align*}
p (f_6 + f_7 + q f_8 + p f_{68} + q f_{78} + r f_{88}) &= (p + 3q + 20r) f_8 + (2q + 10r) f_8 \\
&\Rightarrow (13)
\end{align*}
$$

$$
\begin{align*}
\Rightarrow (13)
\end{align*}
$$

The $r = -0.2$ and $r = -0.6$ are contradictory values. Then the option given by Eq. 12, with $f_{68}$, $f_{78}$, $f_{88}$ is not applicable for checking $f_{ij}$ (Eq. 1) as the criterion of independency of the related balances.

**Formulation of Redox Systems**

**Example 3: We consider here**

1. T subsystem (volume V mL), composed of $KMn\text{O}_4 (N\text{}_{61}) + H\text{}_2O (N\text{}_{62}) + CO\text{}_2 (N\text{}_{63})$

2. D subsystem ($V_0$ mL), composed of $FeSO\text{}_4 7H\text{}_2O (N\text{}_{64}) + H\text{}_2SO\text{}_4 (N\text{}_{65}) + H\text{}_2O (N\text{}_{66}) + CO\text{}_2 (N\text{}_{67})$

and

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

$H\text{}_2O (N_j); H\text{}_2O\text{}_2 (N_j, n_j), OH\text{}^{-2} (N_j, n_j), HSO\text{}_4\text{}^{-1} (N_j, n_j),$ $SO\text{}_4\text{}^{-2} (N_j, n_j), H_2CO\text{}_3 (N_j, n_j), HCO\text{}_3\text{}^{-1} (N_j, n_j),$ $CO\text{}_3\text{}^{-2} (N_j, n_j), Fe\text{}_2 (N_j, n_j), Fe\text{}_2O\text{}_3 (N_j, n_j),$ $FeSO\text{}_4 (N_j, n_j, Fe\text{}_3 (N_j, n_j), FeOH\text{}_2 (N_j, n_j),$ $Fe(OH)\text{}_2 (N_j, n_j), Fe(OH)\text{}_2 (N_j, n_j), FeSO\text{}_4 (N_j, n_j, Fe(SO\text{}_2)\text{}_2 (N_j, n_j), K\text{}_2 (N_j, n_j),$ $MnO\text{}_3 (N_j, n_j), MnO\text{}_3 (N_j, n_j), Mn\text{}_3 (N_j, n_j),$ $MnOH\text{}_2 (N_j, n_j), Mn\text{}_2 (N_j, n_j), MnOH\text{}_2 (N_j, n_j),$ $MnSO\text{}_4 (N_j, n_j).$ (14)

The presence of $CO\text{}_2$ in T and D is considered here as an admixture from air, to imitate real conditions of the analysis, on the step of preparation of D and T; the titration $T(V) \Rightarrow D(V_0)$ is realized in the closed system, under isothermal conditions. Precipitation of MnO$_4$ does not occur at sufficiently low pH value [1].

The D+T dynamic redox system is then composed of non-redox static subsystems: D and T. On this basis, some general properties involved with non-redox and redox systems will be indicated. Different forms of GEB, resulting from linear

$$
\begin{bmatrix}
 f_{68} \\
 f_{78} \\
 f_{88}
\end{bmatrix}
= \begin{bmatrix}
 1 & 0 & 0 \\
 0 & 1 & 2 \\
 0 & 0 & 10
\end{bmatrix}
\begin{bmatrix}
 f_6 \\
 f_7 \\
 f_8
\end{bmatrix}
$$

$$
\begin{align*}
\begin{bmatrix}
 f_{68} \\
 f_{78} \\
 f_{88}
\end{bmatrix}
= \begin{bmatrix}
 0 & 1 & 0 \\
 0 & 0 & 20 \\
 1 & 1 & 0
\end{bmatrix}
\begin{bmatrix}
 f_6 \\
 f_7 \\
 f_8
\end{bmatrix}
\end{align*}
$$
combinations of charge and elemental balances related to D+T system, will be obtained.

To avoid (possible) disturbances, the common notation (subscripts) assumed in the set (14) of species will be applied for components and species in T, D and D+T. In context with the dynamic D+T system, T and D are considered as static (sub)systems.

**Linear combination of balances**

**The T subsystem:** We get here the balances:

\[ f_0 = \text{ChB} \]

\[ N_2 - N_3 - N_\gamma - 2N_\beta + N_{18} - N_{19} = 0 \]

\[ f_1 = f(\text{H}) \]

\[ 2N_1 + N_\gamma(1+2n_\gamma) + N_\delta(1+2n_\delta) + N_\psi(2+2n_\psi) + N_\omega(1+2n_\omega) + 2N_n + 2N_{1\theta n_{1\theta}} + 2N_{\theta n_{1\theta}} = 2N_{n_{1\theta}} \]

\[ f_2 = f(\text{O}) \]

\[ N_\gamma + N_n + N_\delta(1+n_\delta) + N_\psi(3+n_\psi) + N_\omega(3+n_\omega) + N_{1\theta n_{1\theta}} + N_{\theta n_{1\theta}}(4+n_{\theta n_{1\theta}}) = 4N_{n_{1\theta}} + 2N_{\theta n_{1\theta}} - 4N \]

\[ f_3 = -f(\text{Fe}) \]

\[ 4N_{n_{1\theta}} + 4N_{\theta n_{1\theta}} = 0 \]

\[ 0 = 0 \]

i.e., the the linear combination (15) is transformed into identity, 0 = 0. From transformation of (16)

\[ (+1)f_1 + (-2)f_2 + (+4)f_3 + (+6)f_6 + (2)f_7 - f_0 \Rightarrow (+1)f(H) + (-2)f(\text{O}) + (+4)f(\text{CO}) + (+6)f(\text{SO}) + (+2)f(\text{Fe}) - \text{ChB} \]

we see again that the coefficients/multipliers at the balances \( f(Y) \) are equal to ONs of elements in the corresponding species.

**The D subsystem:**

We get here the balances:

\[ f_0 = \text{ChB} \]

\[ N_2 - N_3 - N_\gamma - 2N_\beta + 2N_n + N_{10} + 3N_{12} + 2N_{13} + N_{14} + 4N_{15} + N_{16} - N_{17} + N_{18} - N_{19} - 2N_{20} + 3N_{21} + 2N_{22} + 2N_{23} + N_{24} = 0 \]

\[ f_1 = f(\text{H}) \]

\[ 2N_1 + N_\gamma(1+2n_\gamma) + N_\delta(1+2n_\delta) + N_\psi(1+2n_\psi) + 2N_n + 2N_{1\theta n_{1\theta}} = 2N_{n_{1\theta}} \]

\[ f_2 = f(\text{O}) \]

\[ N_\gamma + N_n + N_\delta(1+n_\delta) + N_\psi(3+n_\psi) + N_\omega(3+n_\omega) + N_{1\theta n_{1\theta}} + N_{\theta n_{1\theta}}(4+n_{\theta n_{1\theta}}) = 4N_{n_{1\theta}} + 2N_{\theta n_{1\theta}} - 4N \]

\[ f_3 = -f(\text{Fe}) \]

\[ 4N_{n_{1\theta}} + 4N_{\theta n_{1\theta}} = 0 \]

\[ 0 = 0 \]

\[ 0 = 0 \]

i.e., the the linear combination (16) is transformed into identity, 0 = 0. From transformation of (16)

\[ (+1)f_1 + (-2)f_2 + (+4)f_3 + (+6)f_6 + (2)f_7 - f_0 \Rightarrow (+1)f(H) + (-2)f(\text{O}) + (+4)f(\text{CO}) + (+6)f(\text{SO}) + (+2)f(\text{Fe}) - \text{ChB} \]

we see again that the coefficients/multipliers at the balances \( f(Y) \) are equal to ONs of elements in the corresponding species.

**The D+T system**

For the D+T system, from (14) we have the balances:

\[ f_0 = \text{ChB} \]

\[ N_2 - N_3 - N_\gamma - 2N_\beta + 2N_n + N_{10} + 3N_{12} + 2N_{13} + N_{14} + 4N_{15} + N_{16} - N_{17} + N_{18} - N_{19} - 2N_{20} + 3N_{21} + 2N_{22} + 2N_{23} + N_{24} = 0 \]

\[ f_1 = f(\text{H}) \]

\[ 2N_1 + N_\gamma(1+2n_\gamma) + N_\delta(1+2n_\delta) + N_\psi(1+2n_\psi) + 2N_n + 2N_{1\theta n_{1\theta}} = 2N_{n_{1\theta}} \]

\[ f_2 = f(\text{O}) \]

\[ N_\gamma + N_n + N_\delta(1+n_\delta) + N_\psi(3+n_\psi) + N_\omega(3+n_\omega) + N_{1\theta n_{1\theta}} + N_{\theta n_{1\theta}}(4+n_{\theta n_{1\theta}}) = 4N_{n_{1\theta}} + 2N_{\theta n_{1\theta}} - 4N \]

\[ f_3 = -f(\text{Fe}) \]

\[ 4N_{n_{1\theta}} + 4N_{\theta n_{1\theta}} = 0 \]

\[ 0 = 0 \]

\[ 0 = 0 \]

\[ 0 = 0 \]
- \( f_5 = -f(Mn) \)

\[
N_{01} = N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} \tag{21}
\]

- \( 6 \cdot f_6 = -6 \cdot f(SO_4^2-) \)

\[
6N_{04} + 6N_{05} = 6N_{06} + 6N_{11} + 6N_{16} + 12N_{17} + 6N_{25} \tag{22}
\]

- \( f_7 = -f(Fe) \)

\[
N_{04} = N_{19} + N_{16} + N_{15} + N_{14} + N_{13} + 2N_{15} + N_{16} + N_{17} \tag{23}
\]

Then we have, by turns,

\[
f_{12} = \frac{2}{3} (O) - (H) \tag{24}
\]

\[
-2N_{03} + 3N_{04} + 7N_{05} + 8N_{06} + 4N_{07} + 5N_{08} + 6N_{10} + N_{12} + 4N_{13} + 2N_{14} + 2N_{15} + 2N_{16} + 2N_{17} + 2N_{18} + 2N_{19} = 8N_{01} + 4N_{03} + 8N_{04} + 6N_{05} + 4N_{07} \tag{25}
\]

\[
f_{12} + f_0 = 4f_5 - f_6 - 6f_7 \tag{26}
\]

\[
2(N_{03} + N_{10} + N_{13}) + 3(N_{12} + N_{13} + N_{20} + N_{21} + N_{23} + N_{24}) + 7N_{19} + 6N_{20} + 3(N_{21} + N_{23}) + 2(N_{22} + N_{23} + N_{25}) = 7N_{01} + 2N_{04} \tag{27}
\]

From transformation of (26) we have

\[
(+1)f_1 + (-2)f_2 + (4+4)f_4 + (+1)f_5 + (+6)f_6 - f_0 \Rightarrow
\]

\[
(+1)f(H) + (-2)f(O) + (4+4)f(CO_2) + (+1)f(K) + (+6)f(SO_2) \tag{28}
\]

We see that the coefficients/multipliers at the related balances \( f_k \) (k=1,2,3,4,6) are equal to ONs of elements in the corresponding species; the balances \( f_1 \) in (28) are related to fans.

Applying the relations:

\[
[\cdot\cdot\cdot](V_0 + V) = 10^3 \cdot N_{02}/N_{19}, CV = 10^3 \cdot N_{02}/N_{19},
\]

\[
C_{01}V_0 = 10^3 \cdot N_{02}/N_{19}, C_{02}V_0 = 10^3 \cdot N_{02}/N_{19},
\]

\[
C_{03}V_0 = 10^3 \cdot N_{02}/N_{19} \tag{29}
\]

we rewrite Eq. (26) in the more explicit form as

\[
2[Fe^{2+}] + [FeOH]^{-} + [FeSO_4^{2-}] + 3[Fe^{3+}] + [FeOH]^{2-} + [Fe(OH)]^{3-} + 2[Fe(OH)_2]^{+} + [Fe(SO_4)]_{2+} + 7[MnO_4^{2-}] + 6[MnO_3^{2-}] + 3[Mn^{2+}] + [MnOH]^{2-} + 2([Mn^{3+}] + [MnSO_4^{2-}]) = (7CV + 2C_{01}V_0)/(V_0 + V) \tag{30}
\]

Eq. (30), obtained from (25,28,29), consists only of the species, where players are involved. Other linear combinations were also used. Applying atomic numbers: \( Z_{Mn} = 25 \) and \( Z_{Fe} = 26 \), we have

\[
\frac{Z_{Fe}}{2}f_{12} + Z_{Mn}f_{04} - \begin{pmatrix} 12 \end{pmatrix} f_{12} + 4f_5 - f_0 = 6f_7
\]

Equation (32) results immediately from the Approach I to GEB, see [6].

The least extended (the most compact) form is as follows

\[
3f_3 + 2f_2 - (f_12 + f_0 - 4f_5 - f_6 - 6f_7);
\]

\[
(N_{03} + N_{10} + N_{13}) - (5N_{19} + 4N_{20} + N_{21} + N_{22}) = N_{01} - 5N_{01} \Rightarrow
\]

\[
[Fe^{2+}] + [FeOH]^{-} + [FeSO_4^{2-}] - (5[MnO_4^{2-}] + 4[MnO_3^{2-}] + [Mn^{2+}] + [MnOH]^{2-})
\]

\[
-(C_{01}V_0 - 5CV)/(V_0 + V) = 0 \tag{33}
\]

Eq. (25) for \( f_{12} \) (24), considered as pr-GEB (Eq. 1), can also be rewritten in terms of concentrations; we have

\[
- [H^{+}] + [OH^{-}] + 7[HSO_4^{2-}] + 8[SO_4^{2-}] + 4[HCO_3^{2-}]
\]

\[
+ 5[H_2CO_3] + 6[CO_3^{2-}] + [FeOH]^{-} + 8[FeS_2O_4^{2-} + [FeOH]^{2-} + 2[Fe(OH)]^{3-} + 8[FeS_2O_4^{2-}] + 16[FeSO_4]_{2+} + 8[MnO_4^{2-}] + 8[MnO_3^{2-}] + [MnOH]^{2-} + 8[MnSO_4^{2-}]
\]

\[
= (8CV + 8C_{01}V_0 + 4CV + 6C_{02}V_0 + 4C_{02}V_0)/(V_0 + V) \tag{34}
\]

Equations 30, 32–34 are equivalent forms of GEB for this system. Other linear combinations of the balances are also admitted/possible for this purpose; none of them are reduced to the identity 0 = 0. However, the shortest Eq. (33), chosen arbitrarily, seems to be the most useful for calculation purposes—for obvious reasons.

The T and D are non redox subsystems of the redox D+T system; this is not the general regularity, of course. In some other systems, D or T or both (D and T) can form redox subsystems. For example, the Br₂ solution considered in [5,6,37,38] is the redox subsystem D; I₂ + KI solution is the redox subsystem T in [39].

**Calculation Procedure for the D+T System**

Completing the set of independent balances

Equation 33 is completed by charge and concentration balances, obtained from Equations 18, 19, 21, 22, 23 and relations (29). We have, by turns,

\[
[H^{+}] - [OH^{-}] - [HSO_4^{2-}] - 2[SO_4^{2-}] - [HCO_3^{-}] - 2[CO_3^{2-}]
\]

\[
+ 2[Fe^{3+}] + [FeOH]^{-} + 3[Fe^{3+}] + 2[FeOH]^{2-} + [Fe(OH)]^{3-} + 4[Fe(OH)_2]^{3-} + [FeS_2O_4^{2-}] - [FeSO_4^{2-}] + [K^{+}] - [MnO_4^{2-}] - 2[MnO_3^{2-}] + 3[Mn^{2+}] + 2[MnOH]^{2-} + [Mn^{3+}] + [MnSO_4^{2-}] = 0 \tag{18a}
\]

\[
[H_2CO_3] + [HCO_3^{-}] + [CO_3^{2-}] - (C_{01}V_0 + C_{02}V_0)/(V_0 + V) = 0 \tag{19a}
\]

\[
[MnO_4^{2-}] + [MnO_3^{2-}] + [Mn^{3+}] + [MnOH]^{2-} + [Mn^{2+}]
\]

\[
+[MnSO_4^{2-}] - CV/(V_0 + V) = 0 \tag{21a}
\]

\[
[HSO_4^{-}] + [SO_4^{2-}] + [FeS_2O_4^{2-}] + 2[FeS_2O_4^{2-}] + [MnSO_4^{2-}] - (C_{01} + C_{02})V_0/(V_0 + V) = 0 \tag{22a}
\]

\[
[Fe^{2+}] + [FeOH]^{-} + [Fe^{3+}] - [FeOH]^{2-} + [Fe(OH)]^{3-} + 2[Fe(OH)_2]^{3-} + [FeS_2O_4^{2-}] + [FeSO_4^{2-}] + 2[FeS_2O_4^{2-}] + [MnS_2O_4^{2-}] + [MnSO_4^{2-}] - (C_{02} + C_{02})V_0/(V_0 + V) = 0 \tag{23a}
\]
\[ \frac{C_v V_o}{(V_o + V)} = 0 \]  
(23a)

The equality (not equation!)

\[ [K^{-1}] = CV/(V_o + V) \]  
(20a)

can enter immediately Eq. 18a like a number, at defined \( V \)-value.

**The set of interrelations for equilibrium constants**

Concentrations of the species involved in the set of 6 equations: 33, 18a, 19a, 21a, 22a, 23a, are compatible with the complete set of equilibrium constants, specified as follows:

\[
\begin{align*}
[H^+] [OH^-] &= 10^{-14.0}; [HSO_4^-] = 10^1.8 [H^+] [SO_4^{2-}]; \\
[H_2CO_3] &= 10^{16.4} [H^+]^2 [CO_3^{2-}]; [HCO_3^-] &= 10^{10.1} [H^+] [CO_3^{2-}]; \\
[Fe^{3+}] &= [Fe^{2+}] 10^{4.5} [Fe^{2+}] [OH^-]; \\
[Fe(OH)_2^{+}] &= 10^{4.5} [Fe^{2+}] [OH^-]; [Fe(OH)_3^{+}] &= 10^{21.7} [Fe^{3+}]^2 [OH^-]; \\
\text{MnO}_4^- &= \text{Mn}^{2+} 10^{5A(E - 1.507)} + 8pH; \\
\text{MnO}_4^{2-} &= \text{Mn}^{2+} 10^{4A(E - 1.743)} + 8pH; \\
\text{Mn}^{3+} &= \text{Mn}^{2+} 10^{A(E - 1.509)}; \\
\text{MnOH}^2+ &= 10^{4.2} [\text{Mn}^{3+}] [OH^-].
\end{align*}
\]  
(35)

The electrode potentials \( E [V] \) are put in context with standard electrode potentials \( E_0 \)i, expressed in SHE scale [40].

6 independent variables, chosen as components of the vector:

\[
x = [x_1, \ldots, x_6]^T = [E, pH, pMn2, pFe2, pSO4, pH2CO3]^T
\]

where \( E \) - potential \( [V] \), \( pH = - \log[H^+] \), \( pMn2 = - \log[Mn^{2+}] \), \( pFe2 = - \log[Fe^{2+}] \), \( pSO4 = - \log[SO_4^{2-}] \), \( pH2CO3 = - \log[H_2CO_3] \).

**Mole fraction as the parameter of D+T system**

All the variables, put in logarithmic scale, are considered as functions of volume \( V \) of the titrant \( T \) added during the titration \( T \Rightarrow D \), \( x_i = x_i(V) \). The \( V \) \([mL]\) is considered as parameter of the D+T system. On this basis, the mole fraction values

\[
\Phi = \frac{CV}{C_v V_o}
\]

are calculated at pre-assumed \( V_o \), \( C \), \( C_v \) values. The \( \Phi \) provides a kind of normalization (independence on \( V_o \) value) in the system, and is taken as the independent variable on the abscissa of the related plots. The knowledge of the \( x_i = x_i(V) \) values, allows also to calculate the concentrations \( [z_i] \) of the different species of the D+T system on the basis of relations (35) and present these changes as plots on the relevant speciation diagrams \( \log [z_i] = \Phi(\phi) \), together with \( E(\Phi) \) and \( pH = \Phi(\phi) \) relationships. Graphical presentation of the data provides an excellent tool for qualitative and quantitative evaluation of processes, occurring at any point of the titration.

All these data for the D+T system are obtained on the basis of calculations realized with use of the MATLAB [1] computer program.

**Computer program**

function \( F = \text{Function}_\text{MnO4}_\text{Fe}(x) \)

global \( V \) \( V_{\text{min}} \) \( V_{\text{step}} \) \( V_{\text{max}} \) \( V_0 \) \( C \) \( C_1 \) \( C_0 \) \( C_01 \) \( C_02 \) \( H \) \( OH \) \( fi \) \( pH \) \( E \)

global \( Kw \) \( pKw \) \( A \) \( K \) \( logK \) \( logKw \) \( logH \) \( logSO4 \) \( logCO3 \)

global \( logH2CO3 \) \( logH2SO4 \) \( logHCO3 \) \( logFe2 \) \( logFe2OH \) \( logFe2SO4 \) \( logFe3 \) \( logFe3OH \) \( logFe3H2O \) \( logFe3SO4 \) \( logFe3H2O \) \( logFe3SO4 \) \( logFe3H2O \) \( logFe3SO4 \) \( logFe3SO4 \)

\( E=x(1); \)
\( pH=x(2); \)
\( Mn2=10.^{-x(3)}; \)
\( Fe2=10.^{-x(4)}; \)
\( SO4=10.^{-x(5)}; \)
\( pH2CO3=10.^{-x(6)}; \)
\( H=10.^{-pH}; \)
\( pKw=14; \)
\( Kw=10.^{-14}; \)
\( OH=Kw/H; \)
\( A=16.9; \)
\( Mn704=Mn2.*10.^(5.*A.*(E-1.507))+8*pH; \)
\( Mn604=Mn2.*10.^(4.*A.*(E-1.743))+8*pH; \)
\( Mn3=Mn2.*10.^(A.*(E-1.509)); \)
\( Fe3=Fe2.*10.^{(A.*(E-0.771))}; \)
\( HSO4=10.^{-1.8.*H.*SO4}; \)
\( CO3=10.^{-1.64.*H.^{2}*H2CO3}; \)
\( HCO3=10.^{10.1.*H.*CO3}; \)
Fe$_2$OH$=10^{4.5}$*Fe$_2$*OH;
Fe$_2$SO$_4$=10^{2.3}*Fe$_2$*SO$_4$;
Fe$_3$OH$=10^{11.0}$*Fe$_3$*OH;
Fe$_3$OH$_2$=10^{21.7}*Fe$_3$*OH.$^2$;
Fe$_3$2OH$_2$=10^{25.1}*Fe$_3$.$^2$*OH.$^2$;
Fe$_3$SO$_4$=10^{4.18}*Fe$_3$*SO$_4$;
Fe$_3$SO$_4$2=10^{7.4}*Fe$_3$*SO$_4$.$^2$;
Mn2OH=10^{3.4}*Mn2*OH;
Mn2SO$_4$=10^{2.28}*Mn2*SO$_4$;
Mn3OH=10^{14.2}*Mn3*OH;
K=C.*V./(V0+V);
K=Fat(1-A);

%Charge balance
F=[(H-OH -HSO$_4$-2.*SO$_4$-HCO$_3$-2.*CO$_3$-+2.*Fe$_2$+Fe$_2$OH... +3.*Fe3+2.*Fe$_3$O3H+Fe$_3$O2H+4.*Fe$_3$2O2H+Fe$_3$SO4-Fe3SO$_4$2... +K-Mn7O4-2.*Mn6O4+3*Mn3+2.*Mn3OH+2.*Mn2+Mn2 OH);

%Concentration balance of Mn
(Mn7O4+Mn6O4+Mn3+Mn3O3H+Mn2+Mn2O2H+Mn2 SO4-C.*V./(V0+V));

%Concentration balance of Fe
(Fe2+Fe2OH+Fe2SO4+Fe3+Fe3OH+Fe3OH2+2.*Fe32 OH2... +Fe3SO4+Fe3SO42-C0.*V0./(V0+V));

%Concentration balance of SO4
(HSO4+SO4+Mn2SO4+Fe2SO4+Fe3SO4+2.*Fe3SO42-(C0+Ca).*V0./(V0+V));

%Concentration balance of CO3
(H2CO3+HCO3+CO3-(C02.*V0+C1.*V)/(V0+V));

%Electron balance
(Fe2+Fe2OH+Fe2SO4-(5.*Mn7O4+4.*Mn6O4+ Mn3+Mn3OH)... -(C0.*V0.-5.*C.*V.)/(V0+V));

logMn2=log10(Mn2);
logMn2OH=log10(Mn2OH);

Figure 1: The relationships: (1a) E = E ( Φ ) and (1b) pH = pH ( Φ ) plotted at (V0, C0, C01, C) = (100, 0.01, 0.5, 0.02) and C1 = C$_{60}$ = 0.

Figure 2: The speciation curves for (2a) Mn species and (2b) Fe species plotted at (V0, C0, C01, C) = (100, 0.01, 0.5, 0.02) and C1 = C$_{60}$ = 0.
logMn$\text{SO}_4$ = log10(Mn$\text{SO}_4$);  
logMn$^3$ = log10(Mn$^3$);  
logMn$^3\text{OH}$ = log10(Mn$^3\text{OH}$);  
logMn$^6\text{O}_4$ = log10(Mn$^6\text{O}_4$);  
logMn$^7\text{O}_4$ = log10(Mn$^7\text{O}_4$);  
logFe$^2$ = log10(Fe$^2$);  
logFe$^2\text{OH}$ = log10(Fe$^2\text{OH}$);  
logFe$^2\text{SO}_4$ = log10(Fe$^2\text{SO}_4$);  
logFe$^3$ = log10(Fe$^3$);  
logFe$^3\text{OH}$ = log10(Fe$^3\text{OH}$);  
logFe$^3\text{OH}_2$ = log10(Fe$^3\text{OH}_2$);  
logFe$^3\text{SO}_4$ = log10(Fe$^3\text{SO}_4$);  
logFe$^3\text{SO}_4^2$ = log10(Fe$^3\text{SO}_4^2$);  
logHSO$^4$ = log10(HSO$^4$);  
logSO$^4$ = log10(SO$^4$);  
logH$\text{2CO}_3$ = log10(H$\text{2CO}_3$);  
logHCO$^3$ = log10(HCO$^3$);  
logCO$^3$ = log10(CO$^3$);  
logK = log10(K);  

Graphical presentation of results and discussion

The results of calculations made at $V_0$ = 100, $C_0$ = 0.01, $C_0$ = 0.5, $C_0$ = 0 are plotted in Figures 1 and 2. The jump of $E$ on the curve in Fig. 1a occurs at $\Phi$ = $\Phi_\text{eq}$ = 0.2, i.e., at the equivalent (eq) point where $C_\text{eq}V_\text{eq} = 0.2C_0V_0$. Relatively small pH changes (Figure 1b) result from high buffer capacity of the titrand D [41-46]. From Figure 2a we see that $[\text{Fe}^{3+}] << [\text{FeSO}_4^{2-}] << [\text{Fe(SO}_4^2)^{-}]$. Note that MnOH$^{2+}$ and Mn$^{3+}$ (not MnO$^4^-$) ions are the predominating manganese species immediately after crossing the related equivalence point (Figure 2b). Some points from the vicinity of equivalence point are presented in Table 1.

Variations on a theme

Option 1. To indicate a complexation effect of sulphate ions, introduced by the H$_2$SO$_4$ solution, we compare the plots of $E = E(\Phi)$ curves: (1) the curve from Fig. 1a with one (2) obtained after omission of the sulfate complexes (FeSO$^4$, FeSO$^4_2$, Fe(SO$^4_4$)$_2^{-}$, MnSO$^4$) from the algorithm in section 4.5. The related plots are compared in Figure 3.

Option 2. The sulphate complexes formed by Mn$^{3+}$ ions are unknown in literature, although on the basis of analogy with other trivalent ions (e.g., Fe$^{3+}$, Al$^{3+}$) it could be expected that the stability constants $K_i$ for virtual Mn(SO$^4_i$)$^{3+}$ complexes, $[\text{Mn(SO}_4^2)^{i-2}] = K_i[\text{Mn}^{3+}][\text{SO}_4^{2-}]$, may have significant values. However, a numerical analysis of the data obtained for the pre-assumed stability constants $K_i$ of sulphate complexes (Figure 4) with the curve obtained experimentally [14] has revealed that the Mn(SO$^4_i$)$^{3+}$ complexes – if they exist – are relatively weak [6].

Final Comments

The quantitative, algebraic description of any electrolytic system according to GATES principles is based on electro neutrality rule, and on rules of conservation of particular elements in the systems, where none radioactive
transformation occurs [2]. The electro-neutrality rule is
expressed by charge balance \( f_i = \mathrm{ChB} \). The conservation of
particular elements is expressed in terms of elemental and
core balances \( f_i = f(Y_i) \), where \( Y_k \) (k = 1, 2, ..., K) is an element
or core. For ordering purposes, it is assumed that \( Y_1 = \mathrm{H} \),
\( Y_2 = 0 \), and the linear combination \( f_{12} = 2 f_2 - f_1 = 2 f(O) - f(H) \) is formulated. In redox systems, \( K \) electron-active
elements/cores (‘fans’), and K-\( K \) electron-active elements
(‘players’) are distinguished. In all examples presented here,
H and O did not participate in redox systems as players. The
set of K balances \( f_{fp1} f_{fp2} f_{p...} f_{pK} \) is needed for mathematical
formulation of a redox system (i.e., at \( K^3 \)), whereas the K-\( \mathrm{K} \)
balances \( f_{fp1} f_{fp2} f_{p...} f_{pK} \) are needed for resolution of a non-redox
system, where \( K^3 = K \) and \( f_{12} \) is the balance linearly dependent
on \( f_{fp1} f_{fp2} f_{p...} f_{pK} \). The linear independency or dependency of
\( f_{12} \) within the balances \( f_{fp1} f_{fp2} f_{p...} f_{pK} \) is then the general,
dichotomous criterion distinguishing between redox and
non-redox systems. The linear combination \( \sum_1^K d_k f_{12} - f_{pK} \) applied to a non-redox system \((1ª) \) gives the identity, \( 0 = 0 \),
for a non-redox system, or \((2 \)º) does not give the identity
for a redox system, also after any linear combination with K-
\( K \) balances for the players in this system. These regularities
are valid for coefficients \( d_k \) equal to oxidation numbers (ONs)
of the elements in the corresponding balances \( f_k = f(Y_k) \) for
elements/cores \( Y_k \) related to fans.

The \( f_{12} \) and any linear combination of \( f_{12} \) with \( f_{fp1} f_{fp2} f_{p...} f_{pK} \)
have full properties of Generalized Electron Balance (GEB),
completing the set of K balances, \( f_{fp1} f_{fp2} f_{p...} f_{pK} \) needed for
resolution of a redox system, of any degree of complexity. The
supreme role of this independency/dependency criterion,
put also in context with calculation of ONs, is of great
importance, in context with the contractual nature of the ON
concept known from the literature issued hitherto [47-49].
These regularities are the clear confirmation of the Emmy
Noether’s general theorem [50] applied to conservation
laws of a physical/electrolytic system, expressed in terms
of algebraic equations, where GEB is perceived as the Law
of Nature [15], as the hidden connection of physicochemical
laws, and as the breakthrough in thermodynamic theory
of electrolytic redox systems. Resolution of several redox
systems, according to principles of Generalized Approach
to Electrolytic Systems (GATES), is presented. The GATES/
GEB is the best thermodynamic approach of electrolytic
redox systems, of any degree of complexity. The Generalized
Equivalent Mass (GEM) concept [14], fully compatible with
the GATES principles, was introduced. The mathematical
tools, applicable for handling the results obtained from
potentiometric titrations in redox systems, were also
presented. The chapter offers – undoubtedly – the best
possible ways to resolution of the issues raised. Formulation
of an electrolytic redox system specified in section 3.1.3
illustrates the huge possibilities/advantages inherent in
GATES/GEB.

All the regularities specified above are valid for redox
and non-redox systems of any degree of complexity, also
for the multi-solvent systems [51-54].

The key role of \( f \) and \( O \) (not free electrons, e \(^{-} \)) in redox
systems, inherent in \( f_{12} \) was stressed in [23]. Contrary
to appearances, established by the current paradigm
“obligatory” till now, the criterion distinguishing non-redox
and redox systems is not immediately associated with free
electrons in the system. The new/fundamental/practical
criterion involved with \( f_{12} = 2 f(O) - f(H) \) and its properties,
unknown in earlier literature, provides a kind of uniformity
in the formulas derived for this purpose. This fact, especially
the simple calculations of free electron concentrations in
redox systems [23], deny the unique role of free electrons in
redox reactions. On the other hand, it points to the decisive
role of \( H \) and \( O \) in redox systems [2], suggested elsewhere,
in earlier theoretical/hypothetical considerations on these
systems. Here is the hidden simplicity, which had to be
discovered, as the Approach II to GEB. The author contends
that the discovery of the Approach II GEB would most likely
be impossible without the prior discovery of the Approach I
to GEB.

The GEB concept, valid for electrolytic redox systems,
is the emanation of balances for \( H \) and \( O \), referred to
aqueous media. GEB is compatible with other (charge
and concentration) balances and enables to resolve the
electrolytic (mono- or/and two-phase) redox systems of any
degree of complexity, within the scope of GATES, perceived
as the thermodynamic approach to equilibrium and
metastable systems, where all necessary physicochemical
knowledge on the systems tested is involved. The GATES is
perceived as the unrivalled tool applicable, among others:
(a) to mathematical modelling of thermodynamic behavior
of the systems, (b) in choice of optimal \( a \) priori conditions of
chemical analyses, and (c) in gaining chemical information
invisible in real experiments, in general.

GATES/GEB is a counter-proposal in relation to earlier
IUPAC decisions, presented in three subsequent editions of
the Orange Book, and based on the reaction stoichiometry;
that viewpoint was criticized unequivocally/exhaustively/
convincingly, especially in a series of authors’ articles cited
herein. It was demonstrated, on examples of redox systems
of different complexity, that stoichiometry is a secondary/
derivative/“fragile” concept, from the viewpoint of GATES,
and GATES/ GEB, in particular.

Conservation laws of physics are very closely related to
the symmetry of physical laws under various transformations.
The nature of these connections is an intriguing physical
problem. The theory of these connections, as it appears
in classical physics, constitutes one of the most beautiful
aspects of mathematical physics. It confirms a general
theorem of Emmy Noether which states that symmetries and
conservation laws of a physical system correspond to each
other [50]. The Noether’s conceptual approach to algebra
led to a body of principles unifying algebra, geometry,
linear algebra, topology, and logic. The theory of this
connection constitutes one of the most beautiful chapters of
mathematical physics.

Concluding, GATES is the overall, thermodynamic
approach to redox and non-redox, static and dynamic,
single and multiphase equilibrium, metastable and non-
equilibrium electrolytic systems, of any degree of complexity.
Possibilities of GATES/GEB are far greater than ones offered by the actual physicochemical knowledge related to the system in question.

Stoichiometry, oxidation number, equivalent mass, order of reaction, equivalent mass [14], etc. are derivative (not primary!) concepts within GATES. The Equilibrium Law (EL), based on the Gibbs function and the Lagrange multipliers idea [15], can be put instead of Mass Action Law (MAL), based on a stoichiometric reaction notation, and other principles. Equilibrium, kinetic and metastable systems are distinguished. Within GATES, thermodynamics of electrolytic systems is based on purely algebraic principles; the stoichiometry is considered here only as a kind of “dummy” [22,23,55].

Summarizing, this paper offers the best possible ways to resolution of the issues raised.

References
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Citation: Michałowski T, Michałowska-Kaczmarszyk AM, (2019) General Properties of the Balance 2/(O)-/(H) in Electrolytic systems. Some Detailed Remarks on Elemental versus Core Balances. J Clin Pharm Vol: 1, Issu: 1 (05-16).