**Research Article**

# Thermodynamic Formulation of Electrolytic Redox Systems According to GATES/ GEB Principles

## Anna M Michałowska-Kaczmarczyk[1], Tadeusz Michałowski[2*]

[1]*Department of Oncology, The University Hospital in Cracow, 31-501 Cracow, Poland*

[2]*Department of Analytical Chemistry, Technical University of Cracow, 31-155 Cracow, Poland*

*\*Corresponding author**
Tadeusz Michałowski, Department of Analytical Chemistry, Technical University of Cracow, 31-155 Cracow, Poland

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## Abstract

*The Generalized Electron Balance (GEB) completes the set of equations needed for quantitative description of an electrolytic redox system. Two equivalent Approaches (I, II) to GEB were formulated in context with the Generalized Approach to Electrolytic Systems (GATES), as GATES/GEB. The Approach I to GEB is based on an electron balance of components and species formed by electron-active elements, termed as players. The Approach II to GEB is based on the linear combination $f_{12} = 2·f(O) – f(H)$ of elemental balances: $f_1 = f(H)$ for $Y_1 = H$, and $f_2 = f(O)$ for $Y_2 = O$. Linear independency/dependency of $f_{12}$ from charge ($f_0 = ChB$) and other elemental/core balances $f_k = f(Y_k)$ (k=3,...,K) for different elements/cores $Y_k$ of the system tested is the general criterion distinguishing between redox and non-redox systems. The GATES / GEB GATES is the best thermodynamic formulation of electrolytic redox systems of any degree of complexity. The GEB is considered as he general law of Nature. Some other/important/basic physicochemical properties inherent in the $f_{21}$ formulation are also indicated. The principle of GATES/GEB formulation is exemplified by the titration $KIO_3 \Rightarrow KI + HCl$.*

**Keywords:** Thermodynamics of Electrolytic Redox Systems, Approach I to GEB, Approach II to GEB, GATES/GEB, Simulation of Dynamic Redox Systems

*Motto 1:* Don't believe anything - but only doubt what is in doubt *(own)*
*Motto 2:* The farther into the forest, the wider the Valley of Obviousness opens *(W. Szymborska)*
*Motto 3:* If a theory cannot be translated into highlander's language, it is a false theory *(J. Tischner)*

## Introduction

In high school and college chemistry curricula, redox reactions are viewed almost exclusively in terms of the chemical reactions notation, considered from stoichiometric viewpoint. Composing (sometimes "sophisticated") summary reaction equations, from a linear combination of partial equations, is a kind of *'l'art* pour l'art'. Sometimes this idea takes degenerate, monstrous forms [1, 2], widely criticized in [3]. However, it was also used to perform simple, stoichiometric calculations [4-6].

Redox systems are the most important and most complex electrolytic systems. The electrolytic redox systems of different complexity, formulated according to Generalized Approach to Redox Systems (GATES) [7-64] were presented in many review articles [16-18, 38-41, 55, 62], and other references cited therein. The simplest redox systems were exemplified in the papers [7-9, 27, 35, 36, 42, 43]. Redox reactions are usually coupled with acid-base, complexation and precipitation reactions [12-15, 31, 32, 41, 55]. Liquid-liquid extraction systems [8] and redox equilibria in multiple solvent media were also considered in this context [24, 63-65].

In this work, the formulation of electrolytic redox systems according to GATES principles is reviewed. Some general properties of electrolytic (non-redox and redox) systems are also indicated. A key role in redox systems plays Generalized Electron Balance (GEB). Two Approaches (I and II) to GEB are presented and illustrated graphically.

The Approach I to GEB is based on a "card game" principle, with electron active elements as "players", electron non-active elements as "fans", and electrons as "money" (see illustration in [29], p. 42). The transmission of electrons/money occurs between the players and does not occur between fans (the fans accounts are intact).

The fundamental property of electrolytic systems is involved with linear combination $f_{12} = 2·f(O) – f(H)$ of elemental balances: $f_1 = f(H)$ for $Y_1 = H$, and $f_2 = f(O)$ for $Y_2 = O$.

The dependence/independence of $f_{12}$ on the set $f_0, f_3, ... f_K$ composed of charge balance ($f_0$=ChB) and other elemental/core balances $f_k = (Y_k)$ (k=3,...,K) is the general criterion distinguishing

between non-redox and redox systems. A core is considered here as a cluster of different atoms with defined composition (expressed by chemical formula), structure and external charge, unchanged in the system in question. For example, $SO_4^{-2}$ is a core within different sulphate components: $FeSO_4 \cdot xH_2O$, $H_2SO_4$ and hydrated species: $HSO_4^{-1}$, $SO_4^{-2}$, $FeSO_4$, $FeSO_4^{+1}$, $Fe(SO_4)_2^{-1}$,, $MnSO_4$ in the D+T titration system $KMnO_4 \Rightarrow FeSO_4 + H_2SO_4$ [62].

## Principles of the Matter and Charge Conservation in Electro lytic Systems

An electrolytic system is perceived as the macroscopic part of the Universe, selected for observation and experimentation. For modeling purposes, realized according to GATES principles, we assume closed system/subsystems,

matter $\nLeftrightarrow$ system/subsystems $\Longleftrightarrow$ heat

separated from its environment by diathermal (freely permeable by heat) walls as boundaries, preventing ($\nLeftrightarrow$) the matter (e.g. $H_2O$, $CO_2$, $O_2$,…) exchange but allowing ($\Longleftrightarrow$) the exchange of heat, resulting from exo- or endothermic processes occurred in there. This way, any process represented by titration, may proceed in quasistatic manner, under isothermal conditions. Constant temperature is one of the conditions securing constancy of equilibrium constants related to the system in question.

We address here to aqueous media, whose species $X_i^{z_i}$ are considered in their natural/factual forms, i.e., as hydrates $X_i^{z_i} \cdot n_{iW}$, where $z_i$ is a charge of this species ($z_i = 0, \pm1, \pm2,…$) expressed in terms of elementary charge unit, $e = F/N_A$ (F – Faraday's constant, $N_A$ – Avogadro's number); $n_{iW}$ ($\geq 0$) is the mean number of water (W=$H_2O$) molecules attached to $X_i^{z_i}$. For these species in aqueous medium, we apply the notation $X_i^{z_i}$ ($N_i$, $n_i$), where $N_i$ is a number of entities of these species in the system, $n_i = n_{iW}$.

Let us assume the electrolytic system formed from $N_{0j}$ (j=1,…,J) molecules of j-th kind as components of the system, with non-radioactive elements involved. The mixture thus obtained involves $N_i$ (i=1,…,I) species of i-th kind.

In order to balance an electrolytic system, two physical laws of conservation are applied, namely:

$1^o$ the law of charge conservation, expressed by charge balance ($f_0$ = ChB), interrelating the numbers $N_i$ of a subset of charged species (ions of i-th kind, $z_i \neq 0$) in the system, and $2^o$ the law of conservation of particular elements/cores $Y_k$ (k=1,…,K), expressing elemental/core balances $f_k = f(Y_k)$, where the numbers $N_{0j}$ of components and the numbers $N_i$ of the species formed in the system are interrelated.

Static and dynamic systems are distinguished. A static system is obtained after a disposable mixing specific chemical compounds as solutes, and water as solvent. A dynamic system can be realized according to titrimetric mode, where – at defined point of the titration – V mL of titrant T is added, in successive portions, into $V_0$ mL of titrand D, and $V_0$+V mL of D+T mixture is thus obtained at this point of the titration, if the volumes are additive; D and T are subsystems of the D+T system.

## Linear Combination of Balances for Electrolytic Systems

For a beginning, let us consider a set of K+1 linear, algebraic equations

$$\sum_{i=1}^{I} a_{ki} \cdot x_i = b_k \Longleftrightarrow \sum_{i=1}^{I} a_{ki} \cdot x_i - b_k = 0 \quad (k = 0,…,K) \tag{1}$$

where $a_{ki}$ are the coefficients, and $b_k$ – free terms. When multiplying Eq. 1 by $\omega_k$, after subsequent summation we have

$$\sum_{k=0}^{K} \omega_k \cdot \sum_{i=1}^{I} a_{ki} \cdot x_i = \sum_{k=0}^{K} \omega_k \cdot b_k \Longleftrightarrow$$

$$\sum_{i=1}^{I} x_i \cdot \sum_{k=0}^{K} \omega_k \cdot a_{ki} = \sum_{k=0}^{K} \omega_k \cdot b_k \tag{2}$$

Assuming

$$b_k = \sum_{j=1}^{J} b_{kj} \cdot x_{0j} \tag{3}$$

from Eqs. 2 and 3 we have

$$\sum_{i=1}^{I} x_i \cdot \sum_{k=0}^{K} \omega_k \cdot a_{ki} = \sum_{j=1}^{J} x_{0j} \cdot \sum_{k=0}^{K} \omega_k \cdot b_{kj} \tag{4}$$

Referring to the problem in question, we assume: $x_i = N_i$, $x_{0j} = N_{0j}$ in Eq. 4, and we write:

$$\sum_{i=1}^{I} N_i \cdot \sum_{k=0}^{K} \omega_k \cdot a_{ki} = \sum_{j=1}^{J} N_{0j} \cdot \sum_{k=0}^{K} \omega_k \cdot b_{kj} \tag{5}$$

The charge balance, $f_0$, is expressed as follows

$$f_0 = \sum_{i=2}^{I} a_{0i} \cdot N_i = \sum_{i=2}^{I} z_i \cdot N_i = 0 \tag{6}$$

where $a_{0i} = z_i$ ; $z_1 = 0$ for $X_1^{z_1} = H_2O$, $z_2 = +1$ for $X_2^{z_2} = H^{+1}$, $z_3 = -1$ for $X_3^{z_3} = OH^{-1}$, … .

The elemental/core balances $f_1 = f(H)$, $f_2 = f(O)$ and $f_k = f(Y_k)$ ($Y_k \neq H, O, k \geq 3,…,K$) are written as follows:

$$f_1 = f(H) = \sum_{i=1}^{I}(a_{1i} + 2n_{iW}) \cdot N_i - \sum_{j=1}^{J} b_{1j} \cdot N_{0j} = 0 \text{ for } Y_1 = H,$$

$$f_2 = f(O) = \sum_{i=1}^{I}(a_{2i} + n_{iW}) \cdot N_i - \sum_{j=1}^{J} b_{2j} \cdot N_{0j} = 0 \text{ for } Y_2 = O,$$

…

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

$$f_K = \sum_{i=1}^{I} a_{Ki} \cdot N_i - \sum_{j=1}^{J} b_{Kj} \cdot N_{0j} = 0$$

where $a_{ki}$ and $b_{kj}$ are the numbers of atoms/cores of k-th element/core in i-th species and j-th component, resp. Then the balance

$$f_{12} = 2 \cdot f_2 - f_1 = 2 \cdot f(O) - f(H) =$$
$$\sum_{i=2}^{I}(2a_{2i} - a_{1i}) \cdot N_i - \sum_{j=1}^{J}(2b_{2j} - b_{1j}) \cdot N_{0j} = 0 \tag{7}$$

is formulated. In the balances $f_0, f_3,…,f_K$ related to aqueous media, the terms involved with water, i.e., $N_{0j}$ (for j related to $H_2O$, as the component), $N_1$, and all $n_i = n_{iW}$ are cancelled within $f_{12}$ (Eq. 7). The linear combination of all K balances: $f_0, f_{12}, f_3,…,f_K$ can be presented in equivalent forms:

$$\sum_{i=1}^{I} N_i \cdot \left(z_i + \sum_{k=1}^{K} \omega_k \cdot a_{ki}\right) = \sum_{j=1}^{J} N_{0j} \cdot \sum_{k=1}^{K} \omega_k \cdot b_{kj} \tag{8a}$$

$$\sum_{i=1}^{I} N_i \cdot z_i + \sum_{k=1}^{K} \omega_k \cdot \left(\sum_{i=1}^{I} N_i \cdot a_{ki} - \sum_{j=1}^{J} N_{0j} \cdot b_{kj}\right) = 0$$

$$f_0 + f_{12} + \sum_{k=3}^{K} \omega_k \cdot f_k = 0$$

$$f_0 + 2 \cdot f_2 - f_1 + \sum_{k=3}^{K} \omega_k \cdot f_k = 0$$

$$d_1 \cdot f(H)) + d_2 \cdot f(O) + \sum_{k=3}^{K} d_k \cdot f(Y_k) - f_0 = 0 \tag{8b}$$

where $d_1 = +1$, $d_2 = -2$, $d_k = -\omega_k$ (k=3,..,K). If all multipliers at $N_i$ and $N_{0j}$ are cancelled simultaneously, from Eq. 8a we have:

$$z_i + \sum_{k=1}^{K} d_k \cdot a_{ki} = 0 \qquad \text{and} \qquad \sum_{k=1}^{K} d_k \cdot b_{kj} = 0$$

for all i and j values (i = 1,…,I; j = 1,…,J), i.e., Eq. 8a is transformed into identity

$$\sum_{i=1}^{I} N_i \cdot 0 = \sum_{j=1}^{J} N_{0j} \cdot 0 \qquad \Leftrightarrow \qquad 0 = 0 \qquad (9)$$

Then transformation of a set of the equations $f_0, f_{12}, f_3, \ldots, f_K$ into the identity, $0 = 0$, proves the linear dependence between these balances in the system considered [32].

Formulation of the proper linear combination, with $d_k$ ($k=1, \ldots, K$) equal to the related oxidation number (ON) values, is then applicable to check the linear dependency or independency of the balances. This way is realized a very useful/effective/desired manner for checking/stating the linear dependence of the balances: $f_0, f_1, f_2, f_3, \ldots, f_K$ related to non-redox systems, named as the transformation of the linear combination $f_0, f_1, f_2, f_3, \ldots, f_K$ to the identity, $0 = 0$ [21, 22]. It is the simplest form of the linear combination for a non-redox system. For a redox system, the proper linear combination of $f_0, f_1, f_2, f_3, \ldots, f_K$, with $d_k$ equal to the related oxidation numbers (ONs), is the way towards the simplest/shortest form of GEB, different from the identity $0 = 0$, Eq. 9.

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

$$f_k = \sum_{i=1}^{I} a_{ki} \cdot N_i - \sum_{j=1}^{J} b_{kj} \cdot N_{0j} = 0 \qquad \Leftrightarrow$$
$$\sum_{i=1}^{I} a_{ki} \cdot N_i = \sum_{j=1}^{J} b_{kj} \cdot N_{0j} \qquad (10)$$

for elements with negative oxidation numbers, or

$$-f_k = \sum_{j=1}^{J} b_{kj} \cdot N_{0j} - \sum_{i=1}^{I} a_{ki} \cdot N_i = 0 \Leftrightarrow$$
$$\sum_{j=1}^{J} b_{kj} \cdot N_{0j} = \sum_{i=1}^{I} a_{ki} \cdot N_i \qquad (11)$$

for elements with positive oxidation numbers, $k \in 3, \ldots, K$. In this notation, $f_k$ will be essentially treated not as the algebraic expression on the left side of the equation $f_k = 0$, but as an equation that can be expressed in alternative forms presented above.

Note, for example, that $f_5 = f(K) \Leftrightarrow f(K) = f_5 \Leftrightarrow -f_5 = -f(K)$. The change of places of numbers $N_i$ for components and $N_{0j}$ for species, see Eqs. 10 and 11, facilitates the purposeful linear combination of the balances, and enables to avoid simple mistakes in this operation.

## Titration $KIO_3 \Rightarrow KI + HCl$

As an example, let us consider the D+T system, where V mL of C mol/L $KIO_3$ is added, as titrant T, into $V_0$ mL of KI ($C_0$) + HCl ($C_{01}$), as titrand D [20], at a given point of the titration. In this system, V mL of T is composed of $N_{01}$ molecules of $KIO_3$ and $N_{02}$ molecules of $H_2O$ and $V_0$ mL of D is composed of $N_{03}$ molecules of KI, $N_{04}$ molecules of HCl, and $N_{05}$ molecules of $H_2O$. In the system thus formed we have the following species:

$H_2O$ ($N_1$), $H^{+1}$ ($N_2$, $n_2$), $OH^{-1}$ ($N_3$, $n^3$), $K^{+1}$ ($N_4$, $n_4$), $I^{-1}$ ($N_5$, $n_5$),

$I_3^{-1}$ ($N_6$, $n_6$), $I_2$ ($N_7$, $n_7$), solid $I_2$ ($N_8$, $n_8$), HIO ($N_9$, $n_9$),

$IO^{-1}$ ($N_{10}$, $n_{10}$), $HIO_3$ ($N_{11}$, $n_{11}$), $IO_3^{-1}$ ($N_{12}$, $n_{12}$), $H_5IO_6$ ($N_{13}$, $n_{13}$), $H_4IO_6^{-1}$ ($N_{14}$, $n_{14}$), $H_3IO_6^{-2}$ ($N_{15}$, $n_{15}$), $Cl^{-1}$ ($N_{16}$, $n_{16}$), $Cl_2$ ($N_{17}$, $n_{17}$), HClO ($N_{18}$, $n_{18}$), $ClO^{-1}$ ($N_{19}$, $n_{19}$), $HClO_2$ ($N_{20}$, $n_{20}$), $ClO_2^{-1}$ ($N_{21}$, $n_{21}$), $ClO_2$ ($N_{22}$, $n_{22}$), $ClO_3^{-1}$ ($N_{23}$, $n_{23}$), $ClO_4^{-1}$ ($N_{24}$, $n_{24}$),

$I_2Cl^{-1}$ ($N_{25}$, $n_{25}$), ICl ($N_{26}$, $n_{26}$), $ICl_2^{-1}$ ($N_{27}$, $n_{27}$). $\qquad (12)$

This notation/numeration will be applied as common in the bal-

ances for D, T and D+T, formulated below. The D and T are considered here as non-redox sub-systems of the redox D+T system. In any non-redox systems, the players are not involved.

## Formulation of Balances for D, T and D+T
### The D subsystem
The balances are as follows:

$f_0 = ChB$

$N_2 - N_3 + N_4 - N_5 - N_{16} = 0$

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + 2N_4n_4 + 2N_5n_5 + 2N_{16}n_{16}$
$= N_{04} + 2N_{05}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4n_4 + N_5n_5 + N_{16}n_{16} = N_{05}$

$f_3 = f(I)$

$N_5 = N_{03}$

$f_4 = f(Cl)$

$N_{16} = N_{04}$

$-f_5 = -f(K)$

$N_{03} = N_4$

Then we get:

$f_{12} = 2f_2 - f_1$

$-N_2 + N_3 = -N_{04}$

$f_{012345} = f_0 + f_{12} + f_3 + f_4 - f_5 \qquad (13)$

$0 = 0$

### The T subsystem
The balances are as follows:

$f_0 = ChB$

$N_2 - N_3 + N_4 - N_{12} = 0$

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + 2N_4n_4 + N_{11}(1+2n_{11}) + 2N_{12}n_{12}$
$= 2N_{02}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4n_4 + N_{11}(3+n_{11}) + N_{12}(3+n_{12}) = 3N_{01}$
$+ N_{02} - 5f_3 = -5f(I)$

$5N_{01} = 5N_{11} + 5N_{12}$

$-f_5 = -f(K)$

$N_{01} = N_4$

Then we get:

$f_{12} = 2f_2 - f_1$

$-N_2 + N_3 + 5N_{11} + 6N_{12} = 6N_{01}$

$f_{01235} = f_0 + f_{12} - 5f_3 - f_5 \qquad (14)$

$0 = 0$

## The D+T system (Approach II to GEB)

The balances are as follows:

$f_0 = ChB$

$N_2 - N_3 + N_4 - N_5 - N_6 - N_{10} - N_{12} - N_{14} - 2N_{15} - N_{16} - N_{19} - N_{21}$
$- N_{23} - N_{24} - N_{25} - N_{27} = 0$ (15)

$f_1 = f(H)$

$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + 2N_4n_4 + 2N_5n_5 + 2N_6n_6 + 2N_7n_7$
$+ 2N_8n_8 + N_9(1+2n_9) + 2N_{10}n_{10} + N_{11}(1+2n_{11}) + 2N_{12}n_{12}$
$+ N_{13}(5+2n_{13}) + N_{14}(4+2n_{14}) + N_{15}(3+2n_{15}) + 2N_{16}n_{16} + 2N_{17}n_{17}$
$+ N_{18}(1+2n_{18}) + 2N_{19}n_{19} + N_{20}(1+2n_{20}) + 2N_{21}n_{21} + 2N_{22}n_{22}$
$+ 2N_{23}n_{23} + 2N_{24}n_{24} + 2N_{25}n_{25} + 2N_{26}n_{26} + 2N_{27}n_{27}$
$= 2N_{02} + N_{04} + 2N_{05}$

$f_2 = f(O)$

$N_1 + N_2n_2 + N_3(1+n_3) + N_4n_4 + N_5n_5 + N_6n_6 + N_7n_7 + N_8n_8$
$+ N_9(1+n_9) + N_{10}(1+n_{10}) + N_{11}(3+n_{11}) + N_{12}(3+n_{12}) + N_{13}(6+n_{13})$
$+ N_{14}(6+n_{14}) + N_{15}(6 + n_{15}) + N_{16}n_{16} + N_{17}n_{17} + N_{18}(1+n_{18})$
$+ N_{19}(1+n_{19}) + N_{20}(2+n_{20}) + N_{21}(2+n_{21}) + N_{22}(2+n_{22}) + N_{23}(3+n_{23})$
$+ N_{24}(4+n_{24}) + N_{25}n_{25} + N_{26}n_{26} + N_{27}n_{27} = 3N_{01} + N_{02} + N_{05}$

$f_3 = f(I)$

$N_5 + 3N_6 + 2N_7 + 2N_8 + N_9 + N_{10} + N_{11} + N_{12} + N_{13} + N_{14} + N_{15}$
$+ 2N_{25} + N_{26} + N_{27} = N_{01} + N_{03}$ (16)

$f_4 = f(Cl)$

$N_{16} + 2N_{17} + N_{18} + N_{19} + N_{20} + N_{21} + N_{22} + N_{23} + N_{24} + N_{25} + N_{26}$
$+ 2N_{27} = N_{04}$ (17)

$- f_5 = - f(K)$

$N_{01} + N_{03} = N_4$ (18)

Then we get:

$f_{12} = 2f_2 - f_1$

$- N_2 + N_3 + N_9 + 2N_{10} + 5N_{11} + 6N_{12} + 7N_{13} + 8N_{14} + 9N_{15} + N_{18}$
$+ 2N_{19} + 3N_{20} + 4N_{21} + 4N_{22} + 6N_{23} + 8N_{24} = 6N_{01} - N_{04}$ (19)

$f_0 + f_{12} - f_5$

$- N_5 - N_6 + N_9 + N_{10} + 5(N_{11}+N_{12}) + 7(N_{13}+N_{14}+N_{15}) - N_{16} + N_{18}$
$+ N_{19} + 3(N_{20}+N_{21}) + 4N_{22} + 5N_{23} + 7N_{24} - N_{25} - N_{27}$

$= 5N_{01} - N_{03} - N_{04}$ (20)

$(f_0 + f_{12} + f_3 + f_4 - f_5)/2$

$N_6 + N_7 + N_8 + N_9 + N_{10} + 3(N_{11}+N_{12}) + 4(N_{13}+N_{14}+N_{15}) + N_{17}$
$+ N_{18} + N_{19} + 2(N_{20}+N_{21}+N_{22}) + 3N_{23} + 4N_{24} + N_{25} + N_{26} + N_{27}$

$= 3N_{01}$ (21)

The terms: $N_{03}$, $N_{04}$, $N_5$ and $N_{16}$ related to iodide and chloride as components and species are not involved in (20). Applying atomic numbers: $Z_I = 53$ for I and $Z_{Cl} = 17$ for Cl, from Eqs. 16, 17 and 19 we have:

$Z_I f_3 + Z_{Cl} f_4 - (f_0 + f_{12} - f_5)$

$(Z_I+1)N_5 + 3Z_I+1)N_6 + 2Z_I(N_7+N_8) + (Z_I-1)(N_9+N_{10})$
$+ (Z_I-5)(N_{11}+N_{12}) + (Z_I-7)(N_{13}+N_{14}+N_{15}) + (Z_{Cl}+1)N_{16} + 2Z_{Cl}N_{17}$
$+ (Z_{Cl}-1)(N_{18}+N_{19}) + (Z_{Cl}-3)(N_{20}+N_{21}) + (Z_{Cl}-4)N_{22} + (Z_{Cl}-5)N_{23}$
$+ (Z_{Cl}-7)N_{24} + (2Z_I+Z_{Cl}+1)N_{25} + (Z_I+Z_{Cl})N_{26} + (Z_I+2Z_{Cl}+1)N_{27}$
$= (Z_I-5)N_{01} + (Z_I+1)N_{03} + (Z_{Cl}+1)N_{04}$ (22)

Linear combinations: $f_0 + f_{12} - f_5$ and $(f_0 + f_{12} + f_3 + f_4 - f_5)/2$ were intended towards obtaining an equation made up of the smallest number of terms. Eq. 20 is obtained from $f_0$ and balances for elements/cores (H, O, K) considered here as fans. Eqs. 20 – 22 include only components and species where players are involved.

Eqs. 19 – 22 are equivalent forms of GEB to the system tested; Eq. 18 is here the primary form of GEB, $f_{12} = pr$-GEB. More-

over, any linear combination of $f_{12}$ with the balances $f_0, f_3, ..., f_5$ has here full properties of GEB for this system.

## A Remark

When formulating the balances $f_1$ and $f_2$, it is possible to take into account the formation of water clusters $(H_2O)_\lambda$ ($N_{1,\lambda}$, $\lambda = 1,2,...$) in aqueous solutions. Writing these balances as follows:

$f_1 = f(H)$
$2 \cdot \sum_{\lambda=1}^{\Lambda} \lambda \cdot N_{1,\lambda} + N_2(1+2n_2) + N_3(1+2n_3) + ...$

$f_2 = f(O)$
$\sum_{\lambda=1}^{\Lambda} \lambda \cdot N_{1,\lambda} + N_2(1+n_2) + N_3(1+n_3) + ...$

we have:
$f_{12} = 2f_2 - f_1$:

$- N_2 + N_3 + ...$

i.e., all components related to the clusters (and water molecules) are cancelled.

## The D+T system (Approach I to GEB)

The Approach I to GEB indicates *a priori* the elements considered as players; these are iodine (I) and chlorine (Cl) in the D+T system. The rightness of this preliminary assumption be confirmed by the Eq. 21 obtained from the Approach II to GEB.

In the D+T system, iodine (in $KIO_3$, KI) and chlorine (in HCl) are the carriers/distributors of the players' electrons. One atom of I has $Z_I$ iodine electrons, and One atom of Cl has $Z_{Cl}$ chlorine electrons. Therefore, $N_{01}$ molecules of $KIO_3$ involve $(Z_I-5) \cdot N_{01}$ iodine electrons, $N_{03}$ molecules of KI involve $(Z_I+1)N_{03}$ iodine electrons, and $N_{04}$ molecules of HCl involve $(Z_{Cl}+1)N_{04}$ chlorine electrons Thus, the total number of iodine and chlorine electrons introduced by $KIO_3$, KI and HCl is $(Z_I-5) \cdot N_{01} + (Z_I+1)N_{03} + (Z_{Cl}+1)N_{04}$. On this basis, we state that:

$N_5$ species $I^{-1} \cdot n_5 H_2O$ involve $(Z_I+1) \cdot N_4$ iodine electrons;
$N_6$ species $I_3^{-1} \cdot n_6 H_2O$ involve $(3Z_I+1) \cdot N_6$ iodine electrons;
$N_7$ species $I_2 \cdot n_7 H_2O$ involve $2Z_I \cdot N_7$ iodine electrons;
$N_8$ species $I_{2(s)} \cdot n_8 H_2O$ involve $2Z_I \cdot N_8$ iodine electrons;
$N_9$ species $HIO \cdot n_9 H_2O$ involve $(Z_I-1) \cdot N_9$ iodine electrons;(s)
$N_{10}$ species $IO^{-1} \cdot n_{10} H_2O$ involve $(Z_I-1) \cdot N_{10}$ iodine electrons;
$N_{11}$ species $HIO_3 \cdot n_{11} H_2O$ involve $(Z_I-5) \cdot N_{11}$ iodine electrons;
$N_{12}$ species $IO_3^{-1} \cdot n_{12} H_2O$ involve $(Z_I-5) \cdot N_{12}$ iodine electrons;
$N_{13}$ species $H_5IO_6 \cdot n_{13} H_2O$ involve $(Z_I-7) \cdot N_{13}$ iodine electrons;
$N_{14}$ species $H_4IO_6^{-1} \cdot n_{14} H_2O$ involve $(Z_I-7) \cdot N_{14}$ iodine electrons;
$N_{15}$ species $H_3IO_6^{-2} \cdot n_{15} H_2O$ involve $(Z_I-7) \cdot N_{15}$ iodine electrons;
$N_{16}$ species $Cl^{-1} \cdot n_{16} H_2O$ involve $2Z_{Cl} \cdot N_{16}$ chlorine electrons;
$N_{17}$ species $Cl_2 \cdot n_{17} H_2O$ involve $2Z_{Cl} \cdot N_{17}$ chlorine electrons;
$N_{18}$ species $HClO \cdot n_{18} H_2O$ involve $(Z_{Cl}-1) \cdot N_{18}$ chlorine electrons;
$N_{19}$ species $ClO^{-1} \cdot n_{19} H_2O$ involve $(Z_{Cl}-1) \cdot N_{19}$ chlorine electrons;
$N_{20}$ species $HClO_2 \cdot n_{20} H_2O$ involve $(Z_{Cl}-3) \cdot N_{20}$ chlorine electrons;
$N_{21}$ species $ClO_2^{-1} \cdot n_{21} H_2O$ involve $(Z_{Cl}-3) \cdot N_{21}$ chlorine electrons;
$N_{22}$ species $ClO_2 \cdot n_{22} H_2O$ involve $(Z_{Cl}-4) \cdot N_{22}$ chlorine electrons;
$N_{23}$ species $ClO_3^{-1} \cdot n_{23} H_2O$ involve $(Z_{Cl}-5) \cdot N_{23}$ chlorine electrons;
$N_{24}$ species $ClO_4^{-1} \cdot n_{24} H_2O$ involve $(Z_{Cl}-7) \cdot N_{24}$ chlorine electrons;
$N_{25}$ species $I_2Cl^{-1} \cdot n_{25} H_2O$ involve $(2Z_I+Z_{Cl}+1) \cdot N_{25}$ iodine+chlorine electrons;
$N_{26}$ species $ICl \cdot n_{26} H_2O$ involve $(Z_I+Z_{Cl}) \cdot N_{26}$ iodine+chlorine-electrons;
$N_{27}$ species $ICl_2^{-1} \cdot n_{27} H_2O$ involve $(Z_I+2Z_{Cl}+1) \cdot N_{27}$ iodine+chlorine electrons.

Comparison of the total numbers of I and Cl electrons in components and species gives the desired/expected Eq. 22. This way, the equivalency of the Approaches: I (discovered 1992) and II (discovered 2005) to GEB is proved.

$$\text{Approach I to GEB} \Leftrightarrow \text{Approach II to GEB}$$

## The Secret Meaning of the Lotus Flower

To paraphrase/recall a Chinese proverb, one can state [20] that "The lotus flower (GEB), lotus leaves (charge and elemental/core balances) and lotus seed (species) come from the same root (fundamental laws of preservation)" [20]. It's worth mention that lotus is among three plants on the planet able to regulate its own temperature and to produce heat through the thermoregulation process. Isn't it, incidentally, an analogy to thermal stability as one of the conditions ensuring the invariability of the equilibrium constants in the titration process? More about these (and other) fascinating lotus properties one can read in [66].



**Figure 1:** The lotus [66].

## The 'Debt of Honor' Principle in The GEB Formulation

As usually happens in the 'card game' practice (Fig. 2a), the players devote to the game only a part of their cash resources. Similarly, in redox reactions, electrons from the valence shells of atoms of electron-active elements may participate as players. The electrons from the valence shell of the reductant atoms are transferred onto the valence shell of the oxidant atoms. However, this restriction to the valence electrons is not required here.

With this in mind, on the basis of Eq. 22 we formulate the linear combination

$z_I f_3 + z_{Cl} f_4 - (f_0 + f_{12} - f_5)$
$(z_I+1)N_5 + 3z_I+1)N_6 + 2z_I(N_7+N_8) + (z_I-1)(N_9+N_{10})$
$+ (z_I-5)(N_{11}+N_{12}) + (z_I-7)(N_{13}+N_{14}+N_{15}) + (z_{Cl}+1)N_{16} + 2z_{Cl}N_{17}$
$+ (z_{Cl}-1)(N_{18}+N_{19}) + (z_{Cl}-3)(N_{20}+N_{21}) + (z_{Cl}-4)N_{22} + (z_{Cl}-5)N_{23}$
$+ (z_{Cl}-7)N_{24} + (2z_I+z_{Cl}+1)N_{25} + (z_I+z_{Cl})N_{26} + (z_I+2z_{Cl}+1)N_{27}$
$= (z_I-5)N_{01} + (z_I+1)N_{03} + (z_{Cl}+1)N_{04}$ (22a)

where $z_I \leq Z_I$, $z_{Cl} \leq Z_{Cl}$. In particular, for $z_I = 0$, $z_{Cl} = 0$, we have the balance:

$- (f_0 + f_{12} - f_5)$
$N_5 + N_6 - N_9 - N_{10} - 5(N_{11}+N_{12}) - 7(N_{13}+N_{14}+N_{15}) + N_{16}$
$- N_{18} - N_{19} - 3(N_{20}+N_{21}) - 4N_{22} - 5N_{23} - 7N_{24} + N_{25} + N_{27}$
$= - 5N_{01} + N_{03} + N_{04}$ (19a)

formally identical with Eq. 20. This way, we recall the card game without 'live cash' but with 'debt of honor'—in not accidental reference to the title of the thriller novel by T. Clancy (Fig. 2b). *Nota bene*, the "Debt of Honor" was published in 1994, like the first 3 papers on GEB [7-9].

## The Distinguishing Role of $f_{12} = 2 \cdot f(O) - f(H)$ in Electrolytic Systems

Linear independency/dependency of $f_{12}$ from charge ($f_0 = ChB$) and other elemental/core balances $f_k = f(Y_k)$ (k=3,...,K) for different elements/cores $Y_k$ is the general criterion distinguishing between redox and non-redox systems. Hence, a redox system is formulated by the set of K independent balances $f_0, f_{12}, f_3,...,f_K$, whereas the set of K–1 independent balances $f_0, f_3,..., f_K$, is used to describe a non-redox system.
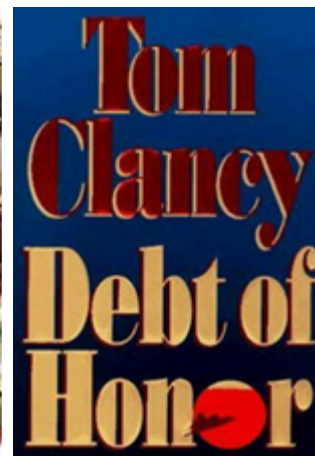


(2a)          (2b)

**Figure 2:** (2a) Card Game [38, 67], and (2b) Debt of Honor [68] as graphical parities of the GEB idea.

## The Balances for D+T System in Terms of Concentrations

The number $N_i$ of the species $X_i^{z_i} \cdot n_i H_2O$ in $V_0+V$ [mL] of the dynamic D+T system, is involved with its molar [mol/L] concentration

$$[X_i^{z_i}] = 10^3 \cdot \frac{N_i}{N_A \cdot (V_0+V)}$$ (23)

Moreover, we have:

$$C \cdot V = 10^3 \cdot \frac{N_{10}}{N_A}, \ C_0 \cdot V_0 = 10^3 \cdot \frac{N_{30}}{N_A}, \ C_{01} \cdot V_0 = 10^3 \cdot \frac{N_{40}}{N_A}$$ (24)

where $N_A$ – Avogadro's number; concentrations are expressed in mol/L, and volumes in mL. Applying (23) and (24) in (15) - (17) and (22), we obtain the equations:

$F_0(x) = [H^{+1}] - [OH^{-1}] + [K^{+1}] - [I^{-1}] - [I_3^{-1}] - [IO^{-1}] - [IO_3^{-1}]$
$- [H_4IO_6^{-1}] - 2[H_3IO_6^{-2}] - [Cl^{-1}] - [ClO^{-1}] - [ClO_2^{-1}] - [ClO_3^{-1}]$
$- [ClO_4^{-1}] - [I_2Cl^{-1}] - [ICl_2^{-1}] = 0$ (15a)

$F_{(1)}(x) = (Z_I+1)\cdot[I^{-1}] + (3Z_I+1)\cdot[I_3^{-1}] + 2Z_I\cdot([I_2] + [I_{2(s)})$
$+ (Z_I-1)\cdot([HIO]+[IO^{-1}]) + (Z_I-5)\cdot([HIO_3]+[IO_3^{-1}])$
$+ (Z_I-7)\cdot([H_5IO_6]+[H_4IO_6^{-1}]+[H_3IO_6^{-2}])$
$+ (Z_{Cl}+1)\cdot[Cl^{-1}] + 2Z_{Cl}\cdot[Cl_2] + (Z_{Cl}-1)\cdot([HClO]+[ClO^{-1}])$
$+ (Z_{Cl}-3)\cdot([HClO_2]+[ClO_2^{-1}]) + (Z_{Cl}-4)\cdot[ClO_2] + (Z_{Cl}-5)\cdot[ClO_3^{-1}]$
$+ (Z_{Cl}-7)\cdot[ClO_4^{-1}] + (2Z_I+Z_{Cl}+1)\cdot[I_2Cl^{-1}] + (Z_I+Z_{Cl})\cdot[ICl]$
$+ (Z_I+2Z_{Cl})\cdot[ICl_2^{-1}] - ((Z_I-5)\cdot CV + (Z_I+1)\cdot C_0V_0$
$+ (Z_{Cl}+1)\cdot C_{01}V_0)/(V_0+V) = 0$ (22a)

$F_3(x) = [I^{-1}] + 3[I_3^{-1}] + 2([I_2] + \mathbf{[I_2]}) + [HIO] + [IO^{-1}] + [HIO_3]$
$+ [IO_3^{-1}] + [H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}] + 2[I_2Cl^{-1}] + [ICl]$
$+ [ICl_2^{-1}] - (C_0V_0 + CV)/(V_0+V) = 0$ (16a)

$F_4(x) = [Cl^{-1}] + 2[Cl_2] + [HClO] + [ClO^{-1}] + [HClO_2] + [ClO_2^{-1}]$
$+ [ClO_2] + [ClO_3^{-1}] + [ClO_4^{-1}] + [I_2Cl^{-1}] + [ICl] + 2[ICl_2^{-1}]$
$- C_{01}V_0/(V_0+V) = 0$ (17a)

The equations 15a, 22a, 16a, 17a: $F_0(x) = 0$, $F_{(I)}(x) = 0$, $F_3(x) = 0$, $F_4(x) = 0$ form a complete set of balances related to the system in question. The values for $C_0$, $C_{01}$, C and $V_0$ are pre-assumed in calculations, V is a steering variable.

The relation $[K^{+1}] = (C_0V_0 + CV)/(V_0+V)$, obtained from Eq. 18, is not considered as the concentration balance, in context with the balances 15a, 21a, 16a, 17a, where more species are involved. At pre-assumed values for $C_0$, $C_{01}$, C, $V_0$ and V (at a given point of titration), $[K^{+1}]$ is a number, not variable, and as such – enters immediately the charge balance 15a in the computer program applied for calculation purposes.

## Equilibrium Constants

In addition to the balances, different species of the system considered are interrelated in expressions for the corresponding equilibrium constants. We have A = F/(RTln10) = 16,9 for T = 298 K, and:

$[H^{+1}] = 10^{-pH}$ ; $[OH^{-1}] = 10^{-14 + pH}$ ; $[I^{-1}] = 10^{-pI}$ ; $[Cl^{-1}] = 10^{-pCl}$;

$[I_2] = [I^{-1}]^2 \cdot 10^{2\cdot A\cdot(E - 0,621)}$; $[I_3^{-1}] = [I^{-1}]^3 \cdot 10^{2\cdot A\cdot(E - 0,545)}$;

$[IO^{-1}] = [I^{-1}]\cdot 10^{2\cdot A\cdot(E - 0,49) + 2\cdot pH - 2\cdot pKw}$;

$[HIO] = [IO^{-1}]\cdot 10^{10,6 - pH}$; $[IO_3^{-1}] = [I^{-1}]\cdot 10^{6\cdot A\cdot(E - 1,08) + 6\cdot pH}$;

$[HIO_3] = [IO_3^{-1}]\cdot 10^{0,79 - pH}$;

$[H_5IO_6] = [I^{-1}]\cdot 10^{8\cdot A\cdot(E - 1,24) + 7\cdot pH}$ ; $[H_4IO_6^{-1}] = [H_5IO_6]\cdot 10^{-3,3 + pH}$;

$[H_3IO_6^{-2}] = [I^{-1}]\cdot 10^{8\cdot A\cdot(E - 0,37) + 9\cdot pH - 9\cdot pKw}$;

$[Cl_2] = [Cl^{-1}]^2 \cdot 10^{2\cdot A\cdot(E - 1,359)}$ ;

$[ClO^{-1}] = [Cl^{-1}]\cdot 10^{2\cdot A\cdot (E - 0,88) + 2\cdot pH - 2\cdot pKw}$;

$[HClO] = [ClO^{-1}]\cdot 10^{7,3 - pH}$ ;

$[ClO_2^{-1}] = [Cl^{-1}]\cdot 10^{4\cdot A\cdot(E - 0,77) + 4\cdot pH - 4\cdot pKw}$;

$[ClO_2] = [Cl^{-1}]\cdot 10^{5\cdot A\cdot(E - 1,5) + 4\cdot pH}$;

$[ClO_3^{-1}] = [Cl^{-1}]\cdot 10^{6\cdot A\cdot(E - 1,45) + 6\cdot pH}$;

$[ClO_4^{-1}] = [Cl^{-1}]\cdot 10^{8\cdot A\cdot(E - 1,38) + 8\cdot pH}$;

$[I_2Cl^{-1}] = [I_2]\cdot 10^{0,2 - pCl}$ ; $[ICl] = [I_2]^{0,5}\cdot 10^{A\cdot(E - 1,105) - pCl}$;

$[ICl_2^{-1}] = [ICl]\cdot 10^{2,2 - pCl}$. (25)

The complete set of equilibrium constants provides the quantitative physicochemical knowledge on the system in question.

Some remark referred to solid iodine, $I_{2(s)}$, as the species with limited solubility $s = 1.33\cdot10^{-3}$ in aqueous media, when put in context with soluble species, $I_2$. So, if total concentration $[I_{2tot}]$ of $I_{2(s)}$ in the system, obtained from calculations, exceeds s, then this excess is put on account of the solid iodine, $[I_{2(s)}] = [I_{2tot}] - s$. If $[I_{2tot}] \leq s$, then $[I_{2(s)}] = 0$. Solubility s of $I_{2(s)}$ is considered in D+T system as one of the equilibrium constants.

## Validity of the General Relation Obligatory for Electrolytic Systems

The simple general relation P = Q + R + 1 between the number P=I of kinds of species, the number Q of (charge, GEB and elemental/core) balances (Q = K for redox or Q = K-1 for non-redox systems) and the number R of independent equilibrium constants related to electrolytic systems, was presented in [69]. This relationship will be confirmed now for the D and T subsystems and for redox D + T system, specified above, namely:

- for D we have: 6 = 1 + 4 + 1
- for T we have: 6 = 2 + 3 + 1
- for D+T we have: 27 = 21 + 5 + 2 (in presence of $I_{2(s)}$), or 26 = 20 + 5 + 1 (in absence of $I_{2(s)}$ as the equilibrium solid phase).

In particular, for T we have Q=K = 2 equilibrium constants: $K_w$ for $H_2O = H^{+1} + OH^{-1}$, and $K_{51}$ for $HIO_3 = H^{+1} + IO_3^{-1}$.

## Oxidation Numbers

The balance $f_0 + f_{12} - f_5$ (Eq. 19) can be rewritten as follows:

$- [I^{-1}] - [I_3^{-1}] + ([HIO]+[IO^{-1}]) + 5([HIO_3]+[IO_3^{-1}])$
$+ 7([H_5IO_6]+[H_4IO_6^{-1}]+[H_3IO_6^{-2}]) - [Cl^{-1}] + ([HClO]+[ClO^{-1}] +$
$3([HClO_2]+[ClO_2^{-1}]) + 4[ClO_2] + 5[ClO_3^{-1}] + 7[ClO_4^{-1}] - [I_2Cl^{-1}]$
$- [ICl_2^{-1}] = 5CV/(V_0+V) - C_0V_0/(V_0+V) - C_{01}V_0/(V_0+V)$ $\Rightarrow$
$(-1)\cdot[I^{-1}] + 3\cdot(-\frac{1}{3})\cdot[I_3^{-1}] + 0\cdot([I_2(s)]+[I_2]) + (+1)\cdot([HIO]+[IO^{-1}])$
$+ (+5)\cdot([HIO_3]+[IO_3^{-1}]) + (+7)\cdot([H_5IO_6]+[H_4IO_6^{-1}] + [H_3IO_6^{-2}])$
$+ (-1)\cdot[Cl^{-1}] + 0\cdot[Cl_2] + (+1)\cdot[HClO] + [ClO^{-1}]$
$+ (+3)\cdot([HClO_2] + [ClO_2^{-1}]) + (+4)\cdot[ClO_2] + (+5)\cdot[ClO_3^{-1}]$
$+ (+7)\cdot[ClO_4^{-1}] + (2\cdot 0 + (-1))\cdot[I_2Cl^{-1}] + ((-1) + 2\cdot 0)\cdot[ICl_2^{-1}]$
$= (+5)\cdot CV/(V_0 + V) + (-1)\cdot C_0V_0/(V_0 + V)$
$+ (-1)\cdot C_01V_0/(V_0 + V)$ (26)

It is worth recalling that oxidation number (ON) is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic, with no covalent component. This is never exactly true for real bonds. A known composition of all the species formed by the players, expressed by their chemical formula and external charge, provides the information sufficient to formulate the related balances. In the Approach II to GEB, none information about a structure of the species is needed. Anyway, the oxidation number, representing the degree of oxidation of an element in a compound or a species, is a contractual concept.

## Calculation Procedure

For the set of four balances (15a), (21a), (16a), (17a) and interrelations (25), one can choose a set of four independent variables (as scalars), forming a vector

$\mathbf{x} = [x(1), x(2), x(3), x(4)]^T = [E, pH, pI, pCl]^T$ (27)

that is a function of V, x = x(V); $^T$ is the transposition sign. On the calculation step, the function

$F(\mathbf{x}(V)) = (F_0(\mathbf{x}(V)))^2 + (F_{(I)}(\mathbf{x}(V)))^2 + (F_3(\mathbf{x}(V)))^2$
$+ (F_4(\mathbf{x}(V)))^2$ (28)

is formulated. The number of variables equals to the number of balances, 4 = 4. The function (27) is then minimized (optimized), at any V-value, according to Optimization Toolbox™ solvers, that start from a set of initial values $x_{start}(V)$ and searches $x(V)$ according to an iterative computer program. This way, the $x = x(V)$ relationships are obtained for different V-values. It enables to calculate concentrations of all species in the system, see the relationships (18). When setting up the calculation algorithm, the modified mathematical setup presented in [27] for HCl titration HCl $\Rightarrow$ NaIO can be used [35, 36].

On this basis, one can plot the functions: $E = E(V)$, $pH = pH(V)$ and speciation curves $\log[X_i^{zi}] = \vartheta_i(V)$. The use of the fraction titrated [70]

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \qquad (29)$$

on the abscissa, provides a kind of normalization in the plots thus obtained, see Fig. 3.

## Graphical Presentation of Results

The main task of a titration is the estimation of the equivalent volume, Veq, corresponding to the volume V of T, where the fraction titrated $\Phi$ (Eq. 22) assumes the value

$$\Phi_{eq} = \frac{C \cdot V_{eq}}{C_0 \cdot V_0} \qquad (30)$$

In contradistinction to visual titrations, where the end volume $V_e \cong V_{eq}$ is registered, see e.g. [30], all instrumental titrations aim, in principle, to obtain the $V_{eq}$ value on the basis of experimental data $\{(V_j, y_j) \mid j=1,\ldots,N\}$, where $y = pH$ or E for potentiometric methods of analysis. We have

$$C_0 \cdot V_0 = 10^3 \cdot \frac{m_A}{M_A} \qquad (31)$$

where $m_A$ [g] and $M_A$ [g/mol] denote mass and molar mass of analyte (A), respectively. From Eqs. 29 and 31, we get

$$m_A = 10^{-3} \cdot C \cdot M_A \cdot \frac{V}{\Phi} \qquad (32)$$

The value of the fraction $V/\Phi$ in Eq. 32, obtained from Eq. 29,

$$\frac{V}{\Phi} = \frac{C_0 \cdot V_0}{C} \qquad (33)$$

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

$$\frac{V}{\Phi} = \frac{V_e}{\Phi_e} = \frac{V_{eq}}{\Phi_{eq}} \qquad (34)$$

The $V_e$ [mL] value is the volume of T consumed up to the end (e) point, where the titration is terminated (ended). The $V_e$ value is usually determined in visual titration, when a pre-assumed color (or color change) of D+T mixture is obtained. In a visual acid-base titration, $pH_e$ value corresponds to the volume $V_e$ [mL] of T added from the very start of the titration, and

$$\Phi_e = \frac{C \cdot V_e}{C_0 \cdot V_0} \qquad (35)$$

is the $\Phi$-value related to the end point. From Eqs. 32 and 34, one obtains:

(a) $\qquad m_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_e} \qquad$ and

(b) $\qquad m_A = 10^{-3} \cdot C \cdot V_{eq} \cdot \frac{M_A}{\Phi_{eq}} \qquad (36)$

This does not mean that we may choose between Eqs. 36a and 36b, to calculate $m_A$. Namely, Eq. 36a cannot be applied for the evaluation of $m_A$: $V_e$ is known, but $\Phi_e$ unknown. Calculation of $\Phi_e$ needs prior knowledge of $C_0$ value. However, $C_0$ is unknown before the titration; otherwise, the titration would be purposeless. Also Eq. 36b is useless: the 'round' $\Phi_{eq}$ value is known exactly, but $V_{eq}$ is unknown; $V_e$ (not $V_{eq}$) is determined in visual titrations. Because Eqs. 36a and 36b appear to be useless, the third, approximate formula for $m_A$, has to be applied [17, 39], namely:

$$m_A' = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_{eq}} \implies m_A' = 10^{-3} \cdot C \cdot V_e \cdot R_A^{eq} \qquad (37)$$
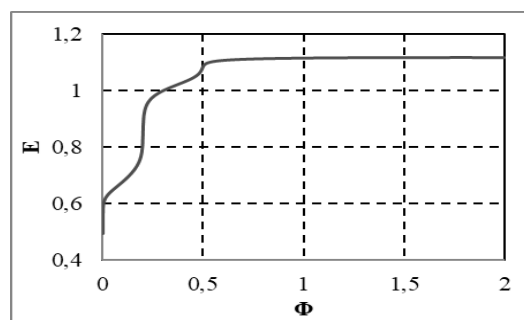
where $\Phi_{eq}$ is put for $\Phi_e$ in Eq. 36a, and
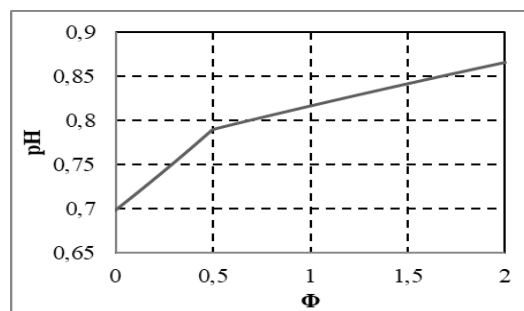
$$R_A^{eq} = \frac{M_A}{\Phi_{eq}} \qquad (38)$$

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

$$\delta = \frac{m_A' - m_A}{m_A} = \frac{m_A'}{m_A} - 1 = \frac{V_e}{V_{eq}} - 1 = \frac{\Phi_e}{\Phi_{eq}} - 1 \qquad (39)$$
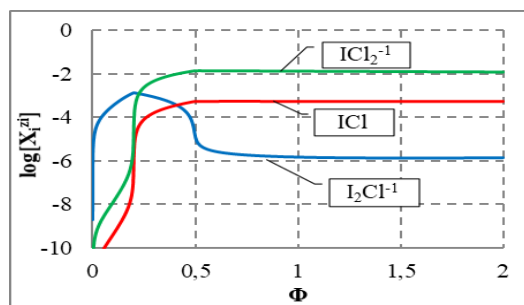
(see examples in [17, 31, 32, 39, 55]).

(3a)

(3b)

(3c)

**Figure 3:** The functions: (3a) $E = E(\Phi)$, (3b) $pH = pH(\Phi)$, and (3c) speciation curves for $I_2Cl^{-1}$, ICl, $ICl_2^{-1}$ at $C_0 = 0.01$, $C = 0.1$.

## Final Comments
### Redundant Terms
In the Approach I to GEB, the knowledge of oxidation numbers of the elements in particular components and species are needed, whereas such a necessity does not occur in the Approach II to GEB. In the Approaches (I, II), the terms: oxidant, reductant are not assigned to any individual species. In the Approach II to GEB, the fans are "filtered" from the set of species (12) in the linear combination $f_0 + f_{12} - f_5$ (Eq. 20), i.e. in algebraic manner, in other words, fans are not stigmatized/categorized arbitrarily as such, and the oxidants, reductants, oxidation numbers (ONs), fans are the redundant/derivative terms within GATES.

### GEM Versus Equivalent Weight - Some Concerns
We will refer here - critically – to the equivalent weight EW (more correctly: equivalent mass) concept. *Nota bene*, the term 'weight' is expressed in the unit of force [N], not mass [g]. In addition, weight – as the force of gravity – depends on the of the gravitational acceleration, which has not the invariant value. Ergo: In the exact sciences, physical terms/units should be used here, and not terms taken straight from the colloquial language.

The EW concept [71] was widely criticized in [3, 17]. As an expressive curiosity one can add the fact that, in 1979, I (TM) tried to publish in Chemia Analityczna my paper criticizing the relevant findings of the IUPAC Commission, contained in [71]; the Editor-in-chief of Chemia Analityczna was then the President of the IUPAC Department of Analytical Chemistry, who prevented my (TM) work from being published; that work eventually appeared in 1981, under a changed title as [72]. Later on, the EW, as gram equivalent weight, was considered as 'abolished term', and as a 'prohibited/ forbidden unit' [73, 74]. However, as can be seen from the current links [75], the EW concept, based on the stoichiometry, is still actual, and "confirmed" by the Richter's portrait placed therein. Nevertheless, the stoichiometry has no mathematical + physical basis, despite the spells uttered by many of its apologists, see the comments in [3, 17].

In this context, the GEM is the best/indisputable/unquestionable option.

The terms: 'substrates' and 'products', commonly used in literature in relation to the notation of a chemical reaction, are inadequate in context with their chemical meaning; 'lefter' and 'righter' seem to be the better proposals, in this regard, when formulating the equilibrium constants.

### The Origins of GEB - Some Personal Concerns
Continuing on the personal thread, I would also like to refer to the circumstances related to the publication of the first works on the Approach I to GEB (this name was introduced later).

The Approach I to GEB was discovered by TM in Feb. 1992. Shortly thereafter 2 papers were prepared by TM and sent together to the Journal of Electroanalytical Chemistry (JEC) Ed. Board. In one of these works, TM referred critically to the work [70] issued in there. The author of this work was selected by the Editor-in-Chief of JEC as the reviewer of both my papers (signed in the reviews); this choice was deliberate (and effec-

tive). The result of the review was short: reject. In this simple (but effective) way, he avoided the criticism of his work. These works were published later, in other journals [7-9]. Therefore, don't bend down for the stone that hit you; keep moving. There has never been an easy time for those who wanted to live honestly. One can also compare the dates of submission (Jan. 6, 1988), and publishing the papers [77, 78].

## Some Concerns on Libre Texts Project
At this point, we will comment the content of some links available on the Internet related to teaching chemistry, usually created for specific academia. There is also aspiration/mission "to unite students, faculty and scholars in a cooperative effort to develop an easy-to-use online platform for the construction, customization, and dissemination of open educational resources (OER) to reduce the burdens of unreasonable textbook costs to our students and society", as stated in the covering information. This mission is realized by the studies of the Chemistry Library https://chem.libretexts.org/ carried out as part of the Libre Texts project [79], and advertised as "the world's most popular online textbook platform". There are, among others, four short texts on acid-base, complexation, precipitation and redox titrations, all dated 2021. Watching the content of the relevant links suggests a sad reflection that the messages contained therein do not differ from the knowledge presented/available over half a century ago. Our objection to this state of affairs we have presented - together with our counterproposals – in our numerous review articles and other thematic studies cited herein, see also Fig 4, as the extension of the one presented in [62].



**Figure 4:** No signature.

All them represent a different, incomparably higher level of subject matter knowledge. Therefore, it is necessary to consider and establish the new convention for presenting teaching materials, consisting in continuous updating of the content of the presented issues based on new solutions in this area. This marks an important /decisive stage in the transition from a chemical language to a mathematical language (Fig. 5).

**Figure 5:** No signature.

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