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AN ELECTROLYTIC REDOX SYSTEM FORMULATED ACCORDING TO GATES/GEB PRINCIPLES

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ABSTRACT

The Generalized Approach to Electrolytic Systems (GATES) provides the best thermodynamic formulation of electrolytic systems of any degree of complexity. When referred to a redox system, it is denoted as GATES/GEB (= GATES), where the Generalized Electron Balance (GEB), considered as the general law of Nature, completes the set of equations needed for quantitative description of such a system. Two equivalent Approaches (I, II) to GEB were formulated. 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 $f_{12} = 2 \cdot f(O) - f(H)$ 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} on charge balance ($f_0 = ChB$) and other elemental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) for different elements/cores Y_k of the system tested is the general criterion distinguishing between redox and non-redox systems. 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 $KIO_3 \rightleftharpoons KI + HCl$.

KEYWORDS thermodynamics of electrolytic redox systems, GATES/GEB, potentiometric titration, simulation of dynamic redox systems..

Introduction

Electrolytic redox and non-redox systems of different complexity were formulated according to Generalized Approach to Electrolytic Systems (GATES) principles. A key role in formulation of redox systems plays Generalized Electron Balance (GEB). Therefore, GATES used for redox systems purposes is denoted more specifically as GATES/GEB. The papers related to GATES/GEB \subset GATES were published in a series of papers [1-54].

Redox reactions are usually coupled with acid-base, complexation and/or precipitation reactions. The simplest redox systems were exemplified in the papers [1-4,17,27,28,34,35]. Liquid-liquid extraction systems [2] and redox equilibria in mixed-solvent media [14] were also considered in this context.

In this work, the formulation of electrolytic systems according to GATES principles is reviewed. Some general properties of electrolytic (non-redox and redox) systems are also indicated. Two Approaches (I and II) to GEB are presented.

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" [30]. The transmission of electrons/money occurs between the players, and does not occur between fans (the fans accounts are intact).

The Approach II to GEB is based on the fundamental property of electrolytic systems, involved with linear combination $f_{12} = 2 \cdot f(O) - f(H)$ 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, \dots, f_k composed of charge balance ($f_0 = ChB$) and other ele-

mental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) 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 $KMnO_4 \rightleftharpoons FeSO_4 + H_2SO_4$ [53].

Principles of the matter and charge conservation in electrolytic 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 $\not\leftrightarrow$ system/subsystems \leftrightarrow heat

separated from its environment by diathermal (freely permeable by heat) walls as boundaries, preventing ($\not\leftrightarrow$) the matter (e.g. H_2O , CO_2 , O_2, \dots) exchange but allowing (\leftrightarrow) the exchange of heat, resulting from exo- or endothermic processes occurred in there. This way, any process represented by titration in aqueous media 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.

The species $X_i^{z_i}$ in aqueous media are considered in their natural/factual forms, i.e., as hydrates $X_i^{z_i} \cdot n_{i,w}$, where z_i is a charge of this species ($z_i = 0, \pm 1, \pm 2, \dots$) expressed in terms of elementary charge

unit, $e = F/N_A$ (F – Faraday's constant, N_A – Avogadro's number); n_{iW} (≥ 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 $X_i^{z_i}(N_i, n_{iW})$, 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} ($j=1, \dots, J$) molecules of j -th kind, termed as components of the system, composed of non-radioactive elements. The mixture thus obtained involves N_i ($i=1, \dots, I$) species of i -th kind, i.e. $X_i^{z_i} \cdot n_{iW}$. In order to balance an electrolytic system, two physical laws of conservation are applied, namely:

1° 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° the law of conservation of particular elements/cores Y_k ($k=1, \dots, K$), 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/single 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

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

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

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

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 $f_k = f(Y_k)$ ($Y_k \neq H, O, k \geq 3, \dots, K$) are written as follows:

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

for $Y_1 = H$,

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

for $Y_2 = O, \dots$

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

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

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

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

is formulated. In the balances f_0, f_3, \dots, f_k related to aqueous media, the terms involved with water, i.e., N_{Oj} (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: $f_0, f_{12}, f_3, \dots, f_k$ can be presented in equivalent forms:

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

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

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

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

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

(8b)

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

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

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

$$\sum_{i=1}^I N_i \cdot 0 = \sum_{j=1}^J N_{Oj} \cdot 0 \quad \Leftrightarrow \quad 0 = 0$$

(9)

Then transformation of a set of the equations $f_0, f_{12}, f_3, \dots, f_k$ 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 ($k=1, \dots, K$) equal to the related oxidation number (ON) values, is then applicable to check the linear dependency or independency of the balances. It is very effective/simplest way of checking/stating the linear dependence of the K balances: $f_0, f_{12}, f_3, \dots, f_k$ related to non-redox systems, named as the transformation of the linear combination of $f_0, f_{12}, f_3, \dots, f_k$ to the identity, $0 = 0$ [11, 12]. It is the simplest form of the linear combination for a non-redox system;. For a redox system, the proper linear combination of $f_0, f_{12}, f_3, \dots, f_k$, with d_k equal to the related oxidation numbers (ONs), is the way towards the simplest/shortest form of GEB, different from the identity $0 = 0$.

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

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

$$\sum_{i=1}^I a_{ki} \cdot N_i = \sum_{j=1}^J b_{kj} \cdot N_{Oj} \quad (10)$$

for elements with negative oxidation numbers, or

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

$$\sum_{j=1}^J b_{kj} \cdot N_{Oj} = \sum_{i=1}^I a_{ki} \cdot N_i \quad (11)$$

for elements with positive oxidation numbers, $k \in 3, \dots, K$. 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.

Titration $KIO_3 \Rightarrow KI + HCl$

As an example, let us consider the D+T system, where V mL of C mol/L KIO₃ is added, as titrant T, into V₀ mL of KI (C₀) + HCl (C₀₁), as titrand D [10], at a given point of the titration. In this system, V mL of T is composed of N₀₁ molecules of KIO₃ and N₀₂ molecules of H₂O and V₀ mL of D is composed of N₀₃ molecules of KI, N₀₄ molecules of HCl, and N₀₅ molecules of H₂O. In the system thus formed we have the following species:

H₂O (N₁), H⁺ (N₂, n₂), OH⁻ (N₃, n₃), K⁺ (N₄, n₄), I⁻ (N₅, n₅), I₃⁻ (N₆, n₆), I₂ (N₇, n₇), solid I₂ (N₈, n₈), HIO (N₉, n₉), IO⁻ (N₁₀, n₁₀), HIO₃ (N₁₁, n₁₁), IO₃⁻ (N₁₂, n₁₂), H₅IO₆ (N₁₃, n₁₃), H₄IO₆⁻ (N₁₄, n₁₄), H₃IO₆⁻² (N₁₅, n₁₅), Cl⁻ (N₁₆, n₁₆), Cl₂ (N₁₇, n₁₇), HClO (N₁₈, n₁₈), ClO⁻ (N₁₉, n₁₉), HClO₂ (N₂₀, n₂₀), ClO₂⁻ (N₂₁, n₂₁), ClO₂ (N₂₂, n₂₂), ClO₃⁻ (N₂₃, n₂₃), ClO₄⁻ (N₂₄, n₂₄), I₂Cl⁻ (N₂₅, n₂₅), ICl (N₂₆, n₂₆), ICl₂⁻ (N₂₇, n₂₇).

(12)

This notation/numeration will be applied as common in the balances for D, T and D+T, formulated below. The D and T are considered here as non-redox subsystems 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:

$$f_0 = \text{ChB}$$

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

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

$$2N_1 + N_2(1+2n_2) + N_3(1+2n_3) + 2N_4n_4 +$$

$$2N_5n_5 + 2N_{16}n_{16} = N_{04} + 2N_{05}$$

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

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

$$f_3 = f(\text{I})$$

$$N_5 = N_{03}$$

$$f_4 = f(\text{Cl})$$

$$N_{16} = N_{04}$$

$$-f_5 = -f(\text{K})$$

$$N_{03} = N_4$$

Then we get:

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

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

$$f_{012345} = f_0 + f_{12} + f_3 + f_4 - f_5$$

(13)

$$0 = 0$$

The T subsystem

The balances are as follows:

$$f_0 = \text{ChB}$$

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

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

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

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

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

$$-5f_3 = -5f(\text{I})$$

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

$$-f_5 = -f(\text{K})$$

$$N_{01} = N_4$$

Then we get:

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

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

$$f_{01235} = f_0 + f_{12} - 5f_3 - f_5$$

(14)

$$0 = 0$$

The D+T system (Approach II to GEB)

The balances are as follows:

$$f_0 = \text{ChB}$$

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

$$f_1 = f(H)$$

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

$$f_2 = f(O)$$

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

$$f_3 = f(I)$$

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

$$f_4 = f(Cl)$$

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

$$-f_5 = -f(K)$$

$$N_{01} + N_{03} = N_4$$

$$(18)$$

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:

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

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

The 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. Moreover, any linear combination of f_{12}

with the balances f_0, f_3, \dots, 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 $(H_2O)_\lambda (N_{1,\lambda}, \lambda = 1, 2, \dots)$ in aqueous solutions. Writing these balances as follows:

$$f_1 = f(H)$$

$$2 \cdot \sum_{\lambda=1}^{\infty} \lambda \cdot N_{1,\lambda} + N_2(1+2n_2) + N_3(1+2n_3) + \dots$$

$$f_2 = f(O)$$

$$\sum_{\lambda=1}^{\infty} \lambda \cdot N_{1,\lambda} + N_2(1+n_2) + N_3(1+n_3) + \dots$$

we have:

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

$$- N_2 + N_3 + \dots$$

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. In this system, iodine (in KIO_3 , KI) and chlorine (in HCl) are the carriers/distributors of the player's 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 $I \cdot n_5H_2O$ involve $(Z_I+1) \cdot N_5$ iodine electrons;

N_6 species $I_3 \cdot n_6H_2O$ involve $(3Z_I+1) \cdot N_6$ iodine electrons;

N_7 species $I_2 \cdot n_7H_2O$ involve $2Z_I \cdot N_7$ iodine electrons;

N_8 species $I_{2(s)} \cdot n_8H_2O$ involve $2Z_I \cdot N_8$ iodine electrons;

N_9 species $HIO \cdot n_9H_2O$ involve $(Z_I-1) \cdot N_9$ iodine electrons;

N_{10} species $IO^- \cdot n_{10}H_2O$ 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 $IO_3^- \cdot n_{12}H_2O$ 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 $H_4IO_6^- \cdot n_{14}H_2O$ 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 $Cl^- \cdot n_{16}H_2O$ 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 $ClO^- \cdot n_{19}H_2O$ 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 $ClO_2^- \cdot n_{21}H_2O$ 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 $ClO_3^- \cdot n_{23}H_2O$ involve $(Z_{Cl}-5) \cdot N_{23}$ chlorine electrons;

N_{24} species $ClO_4^- \cdot n_{24}H_2O$ involve $(Z_{Cl}-7) \cdot N_{24}$ chlorine electrons;

N_{25} species $I_2Cl^- \cdot n_{24}H_2O$ involve $(2Z_I+Z_{Cl}+1) \cdot N_{25}$ iodine+chlorine electrons;

N_{26} species $ICl \cdot n_{24}H_2O$ involve $(Z_I+Z_{Cl}) \cdot N_{26}$ iodine+chlorine electrons;

N_{27} species $ICl_2^- \cdot n_{24}H_2O$ 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 to GEB (discovered 12005) 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 that “The lotus flower (GEB), lotus leaves (charge and elemental/core balances) and lotus seed



Fig. 1. The lotus [55].

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

$$\begin{aligned} & z_i f_3 + z_{Cl} f_4 - (f_0 + f_{12} - f_5) \\ & (z_i + 1)N_5 + 3z_i + 1)N_6 + 2z_i(N_7 + N_8) + (z_i - 1)(N_9 + N_{10}) + (z_i - 5)(N_{11} + N_{12}) + (z_i - 7)(N_{13} + N_{14} + N_{15}) + \\ & (z_{Cl} + 1)N_{16} + 2z_{Cl}N_{17} + (z_{Cl} - 1)(N_{18} + N_{19}) + (z_{Cl} - 3)(N_{20} + N_{21}) + (z_{Cl} - 4)N_{22} + (z_{Cl} - 5)N_{23} + \end{aligned}$$

(species) come from the same root (fundamental laws of preservation)” [10]. It’s worth mentioning, 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 can be read in [55].

$$\begin{aligned} & (z_{Cl} - 7)N_{24} + (2z_i + z_{Cl} + 1)N_{25} + (z_i + z_{Cl})N_{26} + \\ & (z_i + 2z_{Cl} + 1)N_{27} = (z_i - 5)N_{01} + (z_i + 1)N_{03} + \\ & (z_{Cl} + 1)N_{04} \end{aligned} \quad (22a)$$

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

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

formally identical with Eq. 20. This way, we recall the card game without ‘live cash’ but with ‘debt of honor’— in non-accidental analogy with 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 [1-3].



(2a) (2b)
Figure 2. (2a) Card Game [30,56], and (2b) Debt of Honor [57] as graphical parities of the GEB idea.

The distinguishing role of $f_{12} = 2 \cdot f(O) - f(H)$ in electrolytic systems

Linear independency/dependency of f_{12} on charge balance ($f_0 = ChB$) and other elemental/core balances $f_k = f(Y_k)$ ($k=3, \dots, K$) 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 $f_0, f_{12}, f_3, \dots, f_k$, whereas the set of $K-1$ independent balances f_0, f_3, \dots, f_k , is used to describe a non-redox system.

The balances for D+T system in terms of concentrations

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

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

Moreover, we have:

$$C \cdot V = 10^3 \cdot \frac{N_{10}}{N_A}, \quad C_0 \cdot V_0 = 10^3 \cdot \frac{N_{30}}{N_A},$$

$$C_{01} \cdot V_0 = 10^3 \cdot \frac{N_{40}}{N_A} \tag{24}$$

where N_A – Avogadro's number; concentrations are expressed in mol/L, and vol-

umes in mL. Applying (23) and (24) in (15) - (17) and (22), we obtain the equations:

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

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

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

$$F_4(\mathbf{x}) = [Cl^{-1}] + 2[Cl_2] + [HClO] + [ClO^{-1}] + [HClO_2] + [ClO_2^{-1}] + [ClO_2] + [ClO_3^{-1}] + [ClO_4^{-1}]$$

$$+ [I_2Cl^{-1}] + [ICl] + 2[ICl_2^{-1}] - C_0V_0/(V_0+V) = 0$$

(17a)

The equations 15a, 22a, 16a, 17a: $F_0(\mathbf{x}) = 0$, $F_{(1)}(\mathbf{x}) = 0$, $F_3(\mathbf{x}) = 0$, $F_4(\mathbf{x}) = 0$ 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, i.e., $F_0(\mathbf{x}) = [H^{+1}] - [OH^{-1}] + (C_0V_0 + CV)/(V_0+V) - [I^{-1}] - \dots$.

Equilibrium constants

In addition to the balances, different species of the system considered are interrelated in expressions for the corresponding equilibrium constants [10]. We have $A = F/(RT \ln 10) = 16,9$ 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 $s = 1.33 \cdot 10^{-3}$ 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 $I = B + L + 1$ between the number I of kinds of species, the number B of charge balance and elemental/core balances and the number L of independent equilibrium constants related to electrolytic systems, was presented in [25]. $L = K$ for a redox system and $L = K - 1$ for a non-redox system.

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

Oxidation numbers

From Eqs. 19, 23 and 24 we have::

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

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, no 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.

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

and 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, players (oxidants, reductants) and fans are not stigmatized/categorized arbitrarily as such, and the oxidants, reductants, oxidation numbers (ONs), are the redundant/derivative terms within GATES.

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; 'leftier' and 'rightier' seem to be the better proposals in this regard, when formulating the equilibrium constants.

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

$$(27)$$

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

$$\begin{aligned}
 F(\mathbf{x}(V)) = & (F_0(\mathbf{x}(V)))^2 + (F_{(1)}(\mathbf{x}(V)))^2 + \\
 & (F_3(\mathbf{x}(V)))^2 + (F_4(\mathbf{x}(V)))^2 \\
 & (28)
 \end{aligned}$$

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 $\mathbf{x}_{start}(V)$ and searches $\mathbf{x}(V)$ according to an iterative computer program. This way, the $\mathbf{x} = \mathbf{x}(V)$ 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 for HCl titration $\text{HCl} \rightleftharpoons \text{NaIO}$ can be used [27,28].

On this basis, one can plot the functions: $E = E(V)$, $\text{pH} = \text{pH}(V)$ and speciation curves $\log[X_i^{z_i}] = \theta_i(V)$. The use of the fraction titrated [4-6,58,59]

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \tag{29}$$

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

Graphical presentation of results

The relationships: $E = E(\Phi)$ (Fig. 3a), $\text{pH} = \text{pH}(\Phi)$ (Fig. 3b), $\log[X_i^{z_i}] = \theta_i(\Phi)$ (Fig. 4), were obtained for $V_0 = 10$, $C_0 = 0.01$, $C_{01} = 0.2$, $C = 0.1$. For more details - see [11].

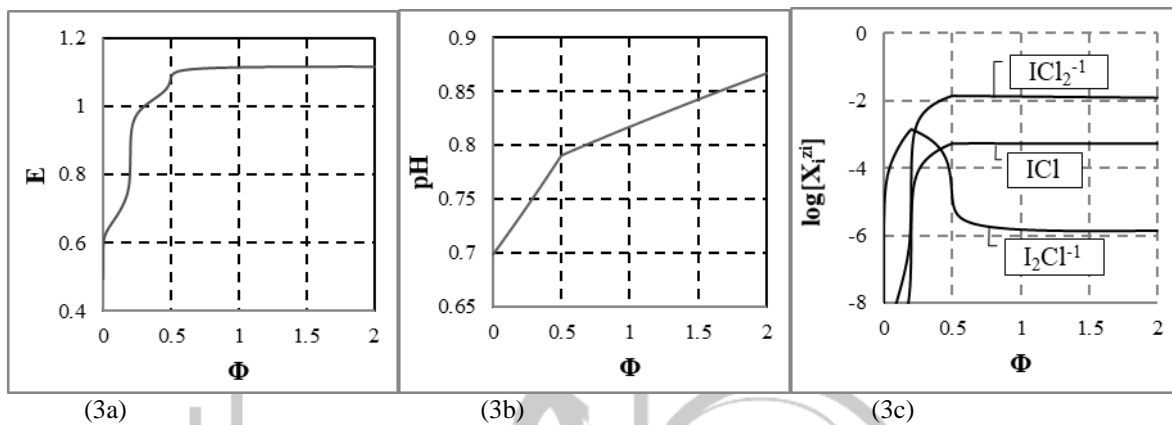


Figure 3. The functions: (3a) $E = E(\Phi)$, (3b) $\text{pH} = \text{pH}(\Phi)$, and (3c) speciation curves for I_2Cl^{-1} , ICl , ICl_2^{-1} , at $C_0 = 0.01$, $C = 0.1$.

Generalized equivalence mass (GEM)

The main task of a titration is the estimation of the equivalent volume, V_{eq} , corresponding to the volume V of T , where the fraction titrated Φ (Eq. 22) assumes the value

$$\Phi_{\text{eq}} = \frac{C \cdot V_{\text{eq}}}{C_0 \cdot V_0} \tag{30}$$

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

$$C_0 \cdot V_0 = 10^3 \cdot \frac{m_A}{M_A} \tag{31}$$

where m_A [g] and M_A [g/mol] denote mass and molar mass of analyte (A), respectively. From Eqs. 22 and 31, we get

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

The value of the fraction $\frac{V}{\Phi}$ in Eq. 32, obtained from Eq. 22,

$$\frac{V}{\Phi} = \frac{C_0 \cdot V_0}{C} \tag{33}$$

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

$$\frac{V}{\Phi} = \frac{V_e}{\Phi_e} = \frac{V_{\text{eq}}}{\Phi_{\text{eq}}} \tag{34}$$

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

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

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

$$(a) \quad m_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_e} \quad \text{and} \quad (b) \\ m_A = 10^{-3} \cdot C \cdot V_{eq} \cdot \frac{M_A}{\Phi_{eq}} \quad (36)$$

This does not mean that we may choose between Eqs. 36a and 36b, to calculate m_A . That is, Eq. 36a cannot be applied for the evaluation of m_A : V_e is known, but Φ_e unknown. Calculation of Φ_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' Φ_{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 [8], namely:

$$m'_A = 10^{-3} \cdot C \cdot V_e \cdot \frac{M_A}{\Phi_{eq}} \Rightarrow \\ m'_A = 10^{-3} \cdot C \cdot V_e \cdot R_A^{eq} \quad (37)$$

where Φ_{eq} is put for Φ_e in Eq. 36a, and

$$R_A^{eq} = \frac{M_A}{\Phi_{eq}} \quad (38)$$

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

$$\delta = \frac{m'_A - m_A}{m_A} = \frac{m'_A}{m_A} - 1 = \frac{V_e}{V_{eq}} - 1 = \frac{\Phi_e}{\Phi_{eq}} - 1 \quad (39)$$

(see examples in [6,23,31,47]). The GEM was suggested in 1979, and presented first time in [58].

The GEM formulation presented above was the counterproposal to IUPAC recommendations [60], where the equivalent weight (EW) concept was recommended. *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 gravitational acceleration, which has not the invariant value. Therefore, in the exact sciences, physical terms/units should be used here, and not terms taken straight from the colloquial language. Later on, the EW, as gram equivalent weight, was considered as abolished term [61], and as a prohibited/forbidden unit. However, the EW concept, based on the stoichiometry, is still actual. The EW concept was widely criticized in [6,21]. In this context, the GEM is the best/indisputable/unquestionable option.

Final comments

In conclusion, we refer critically to the content of the links available on the Internet related to teaching chemistry, usually created for specific academia. There is also a "mission", realized by the the Chemistry Library, carried out as part of the LibreTexts Project [62], 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 level of knowledge contained therein does not differ substantially from the knowledge available over half a century ago, see also Fig 4, as the

extension of the one illustrated graphically in [54].

The knowledge on GATES, and GATES/GEB in particular, exemplified in this paper, refers to an important / decisive stage in the transition of

thermodynamics of electrolytic systems from the current state to algebra, perceived from mathematical, not chemical viewpoint, as noticed/emphasized in [21].

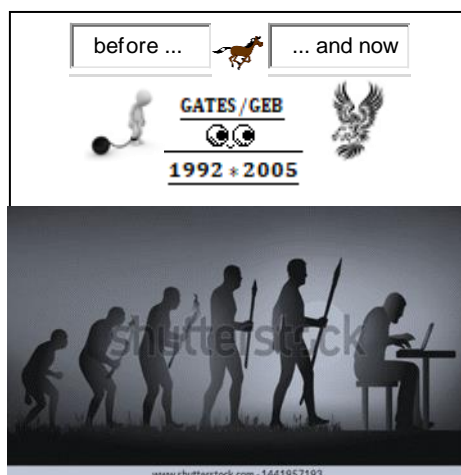


Fig. 4. No signature.

REFERENCES

[1] Michałowski T (1994) Calculation of pH and Potential E for Bromine Aqueous Solution, *J. Chem. Educ.* 71: 560-562.

[2] Michałowski T, Lesiak A (1994) Acid-base titration curves in disproportionating redox systems, *J. Chem. Educ.* 71(8): 632-536.

[3] Michałowski T, Lesiak A (1994) Formulation of generalized equations for redox titration curves. *Chem. Anal. (Warsaw)* 39:623-637.

<http://beta.chem.uw.edu.pl/chemanal/PDFs/1996/CHAN1996V0041P00667.pdf>

[4] Michałowski T, Wajda N, Janecki D. (1996) A unified quantitative approach to electrolytic systems. *Chem. Anal. (Warsaw)*. 41:667-685.

<http://www.chem.uw.edu.pl/chemanal/PDFs/1996/CHAN1996V0041P00667.pdf>

[5] Michałowski T (2010) The Generalized Approach to Electrolytic Systems: I. Physi-

cochemical and Analytical Implications, *Crit. Rev. Anal. Chem.* 40(1): 2-16.

[6] Michałowski T, Pietrzyk A, Ponikvar-Svet M, Rymanowski M (2010) The Generalized Approach to Electrolytic Systems: II. The Generalized Equivalent Mass (GEM) Concept, *Crit. Rev. Anal. Chem.* 40(1): 17-29.

[7] Michałowski T (2011) Application of GATES and MATLAB for Resolution of Equilibrium, Metastable and Non-Equilibrium Electrolytic Systems, Chap. 1: 1 – 34 in: *Applications of MATLAB in Science and Engineering* (ed. by T. Michałowski), InTech - Open Access publisher in the fields of Science, Technology and Medicine.

[8] Michałowski T, Rymanowski M, Pietrzyk A (2005) Nontypical Brønsted Acids and Bases, *J. Chem. Educ.* 82 (3), 470-472.

[9] Michałowski T, Ponikvar-Svet M, Asuero AG, Kupiec K (2012) Thermodynamic and kinetic effects involved with pH titration of

As(III) with iodine in a buffered malonate system, *J. Solution Chem.* 41(3): 436-446.

[10] Michałowski T, Toporek M, Michałowska-Kaczmarczyk AM, Asuero AG (2013) New Trends in Studies on Electrolytic Redox Systems, *Electrochim. Acta* 109: 519–531.

[11] Michałowski T, Michałowska-Kaczmarczyk AM, Toporek M (2013) Formulation of general criterion distinguishing between non-redox and redox systems, *Electrochim. Acta* 112: 199-211.

[12] Michałowska-Kaczmarczyk AM, Michałowski T (2013) Comparative balancing of non-redox and redox electrolytic systems and its consequences, *American Journal of Analytical Chemistry* 4(10): 46-53.

[13] Michałowska-Kaczmarczyk AM, Michałowski T (2014) GATES as the Unique Tool for Simulation of Electrolytic Redox and Non-Redox Systems, *J. Anal. Bioanal. Tech.* 5(4): 1-5, 204. doi: 10.4172/2155-9872.1000204

<https://www.omicsonline.org/open-access/gates-as-the-unique-tool-for-simulation-of-electrolytic-redox-and-non-redox-systems-2155-9872.1000204.php?aid=31166>

[14] Michałowska-Kaczmarczyk AM, Michałowski T (2014) Generalized Electron Balance for Dynamic Redox Systems in Mixed-Solvent Media, *Journal of Analytical Sciences, Methods and Instrumentation* 4(4): 102-109.

[15] Michałowska-Kaczmarczyk AM, Rymanowski M, Asuero AG, Toporek M, Michałowski T (2014) Formulation of Titration Curves for Some Redox Systems, *American Journal of Analytical Chemistry* 5: 861-878.

[16] Michałowska-Kaczmarczyk AM, Michałowski T (2014) Compact formulation of redox systems according to GATES/GEB principles, *Journal of Analytical Sciences, Methods and Instrumentation* 4(2): 39-45.

[17] Toporek M, Michałowska-Kaczmarczyk AM, Michałowski T (2014) Disproportionation Reactions of HIO and NaIO in Static and Dynamic Systems, *American Journal of Analytical Chemistry* 5: 1046-1056.

[18] Michałowski T (2014). Generalized electron balance (GEB) as a law of preservation for electrolytic redox systems. In: 65th Annual Meeting of the International Society of Electrochemistry. Lausanne, Switzerland.

[19] Michałowska-Kaczmarczyk AM, Toporek M, Michałowski T (2015) Speciation Diagrams in Dynamic Iodide + Dichromate System, *Electrochim. Acta* 155: 217–227.

[20] Toporek M, Michałowska-Kaczmarczyk AM, Michałowski T (2015) Symproportionation versus Disproportionation in Bromine Redox Systems, *Electrochim. Acta* 171: 176–187.

[21] Michałowska-Kaczmarczyk AM, Asuero AG, Michałowski T (2015) “Why not stoichiometry” versus “Stoichiometry – why not?” Part I. General context, *Crit. Rev. Anal. Chem.* 45(2): 166–188.

[22] Michałowska-Kaczmarczyk AM, Asuero AG, Toporek M, Michałowski T (2015) “Why not stoichiometry” versus “Stoichiometry – why not?” Part II. GATES in context with redox systems, *Crit. Rev. Anal. Chem.* 45(3): 240–268.

[23] Michałowska-Kaczmarczyk AM, Michałowski T, Toporek M, Asuero AG (2015) “Why not stoichiometry” versus

"Stoichiometry – why not?" Part III, Extension of GATES/GEB on Complex Dynamic Redox Systems, *Crit. Rev. Anal. Chem.* 45(4): 348-366.

[24] Michałowska-Kaczmarczyk AM, Michałowski T, Toporek M, Pietrzyk A (2015) Solubility and Dissolution in Terms of Generalized Approach to Electrolytic Systems Principles, *Journal of Analytical Sciences, Methods and Instrumentation* 5: 47-58.

[25] Michałowska-Kaczmarczyk AM, Michałowski T (2015) General Relation Valid for Electrolytic Systems, *Journal of Analytical Sciences, Methods and Instrumentation* 5: 74-85.

[26] Michałowska-Kaczmarczyk AM, Michałowski T, Toporek M (2016) Formulation of Dynamic Redox Systems according to GATES/GEB Principles, *Int. J. Electrochem.* 11: 2560-2578.

[27] Meija J, Michałowska-Kaczmarczyk AM, Michałowski T (2017) Redox titration challenge, *Anal. Bioanal. Chem.* 409(1): 11-13.

[28] Michałowski T, Michałowska-Kaczmarczyk AM, Meija J (2017) Solution of redox titration challenge, *Anal. Bioanal. Chem.* 409(17): 4113-4115.

[29] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) A general property differentiating between redox and non-redox electrolytic systems and its consequences, *International Journal of Mathematics and Statistics Invention* 5(3): 67-76.

[30] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Generalized Electron Balance (GEB) as the Law of Nature in Electrolytic Redox Systems, in: *Redox: Principles and Ad-*

vanced Applications, Ali Khalid, M.A. (Ed.) *InTech Chap. 2: 9-55.*

[31] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Principles of Titrimetric Analyses According to Generalized Approach to Electrolytic Systems (GATES), in: *Advances in Titration Techniques*, Vu Dang Hoang (Ed.) *InTech Chap. 5: 133-171.*

[32] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) A Distinguishing Feature of the Balance $2 \cdot f(O) - f(H)$ in Electrolytic Systems. The Reference to Titrimetric Methods of Analysis, in: *Advances in Titration Techniques*. Vu Dang Hoang (Ed.) *InTech Chap. 6: 173-207.*

[33] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Solubility products and solubility concepts, in: *Descriptive Inorganic Chemistry. Researches of Metal Compounds*. Akitsu T. (Ed.) *InTech Chap. 5: 93-134.*

[34] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Dynamic Buffer Capacities in Redox Systems, *Appl. Chem. Eng.* 1(2): 1 - 7.

[35] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Dynamic Buffer Capacities in Redox Systems, *Biochem. Mol. Biol. J.* 3(3):1-7.

[36] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Formulation of simple electrolytic redox systems according to GATES/GEB principles, *Journal of Chemistry and Applied Chemical Engineering*, 1(1): 1-10.

[37] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Oxidation number, oxidant and reductant as derivative concepts within GATES/GEB formulation, *Journal of Chem-*

istry and Applied Chemical Engineering, 1: 2-8.

[38] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) Some Regularities Involved with Oxidation Numbers Stated in Formulation of Redox Systems According to GATES/GEB Principles, *J. Anal. Bioanal. Sep. Tech.* 2(2): 102-110.

[39] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2017) General Properties of the Balances $2 \cdot f(O) - f(H)$ Related to Electrolytic Systems, *Analytical Chemistry: An Indian Journal*, 17(2): 124-147.

[40] Michałowska-Kaczmarczyk AM., Michałowski T (2018) Disproportionation and Symproportionation of Bromine formulated according to GATES/GEB Principles, *World Journal of Biology and Medical Sciences* 5(3): 27-45.

[41] Michałowska-Kaczmarczyk AM, Michałowski T (2018) The modified Gran methods in potentiometric redox titrations derived according to GATES/GEB principles, *J. Chem. Eng. Bioanal. Chem.* 2(1): 88-113.

[42] Michałowska-Kaczmarczyk AM, Michałowski T (2018) A compact, algebraic formulation of disproportionation and symproportionation in Bromine systems. *Journal of Chemical Technology and Applications*, 2(2): 1-14.

[43] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T (2018) The balance $2 \cdot f(O) - f(H)$ as a keystone in formulation of electrolytic systems, *Research and Reviews in Computational Chemistry*, 1(1): 1-9.

[44] Michałowska-Kaczmarczyk AM, Michałowski T (2018) The Balance $2 \cdot f(O) - f(H)$ as a Cornerstone in Formulation of

Electrolytic Systems, *Journal of New Developments in Chemistry*, 2(1): 1-13.

[45] Michałowska-Kaczmarczyk AM, Michałowski T (2018) The importance of linear algebra in theory of electrolytic systems, *Austin Chem. Eng.* 5(1): id1060 (001-011).

[46] Michałowska-Kaczmarczyk AM, Michałowski T (2018) "The distinguishing role of $2 \cdot f(O) - f(H)$ in electrolytic systems", *Biomed. J. Sci. Tech. Res.* 8(1): 1-10.

[47] Michałowska-Kaczmarczyk AM, Michałowski T (2019) The new paradigm in thermodynamic formulation of electrolytic systems – A review. *Arch. Biomed. Sci. Eng.* 5(1): 19-61.

[48] Michałowska-Kaczmarczyk AM, Michałowski T (2019) GATES/GEB as the New Paradigm for Electrolytic Redox Systems. *Current Scientific Research in Biomedical Sciences*, 2(1): 1-3.

[49] Michałowska-Kaczmarczyk AM, Michałowski T (2019) General Properties of the Balance $2f(O) - f(H)$ in Electrolytic systems. Some Detailed Remarks on Elemental versus Core Balances, *Journal of Clinical Pharmacy* 1(1): 5-16.

[50] Michałowska-Kaczmarczyk AM, Michałowski T (2019) A dynamic redox system with ascorbic acid formulated and simulated according to GATES/GEB principles, *Current Topics in Analytical Chemistry*, 11: 31-41.

[51] Michałowska-Kaczmarczyk AM, Michałowski T (2020) Justification of Generalized Electron Balance (GEB) as the Law of Nature (Editorial), *Advances in Chemistry and Chemical Technology*, 1(1): 1-3.

[52] Michałowska-Kaczmarczyk AM, Michałowski T (2020) Formulation of metastable redox systems according to

GATES/GEB principles. Simulated Ascorbinometric Titration of Ferricyanide, *Acta Scientific Biotechnology*, 1(2): 1-8.

[53] Michałowska-Kaczmarczyk AM, Michałowski T (2020), GATES/GEB as the Best Thermodynamic Approach to Electrolytic Redox Systems - A Review, *Journal of New Developments in Chemistry*, 3(2): 1-17.

[54] Michałowska-Kaczmarczyk AM, Michałowski T (2021) Some regularities inherent in the balance $2 \cdot f(O) - f(H)$ formulated for an electrolytic system with symproportionation reactions involved, *Academic Journal of Chemistry*, 6(1): 1-11.

[55] Sacred lotus may hold secret of longevity.

[56] Commuter Card Game by Constantin Alajalov, March 15, 1947, *The Saturday Evening Post*.

[57] Debt of Honor by Tom Clancy (1994, Hardcover).

[58] Michałowski T (1981) Some remarks on acid-base titration curves. *Chem. Anal. (Warsaw)* 26:799–813.

[59] Asuero AG, Michałowski T (2011) Comprehensive formulation of titration curves referred to complex acid-base systems and its analytical implications, *Critical Reviews in Analytical Chemistry* 41(2): 151-187.

[60] West TS (1978) Recommendations on the usage of the terms 'equivalent' and 'normal.' *Pure Appl. Chem.* 50:325–338.

[61] Zhao M, Lu I (1994) Abolition of the equivalent. Rule of equal amount of substance. *Anal. Chim. Acta* 289:121–124.

[62] LibreTexts, LibreTexts