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Formulation of general criterion distinguishing between non-redox and redox systems

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ABSTRACT

The paper provides a comprehensive, compatible and consistent approach to thermodynamics of electrolytic redox and non-redox systems, referred to aqueous, non-aqueous and mixed-solvent media. It is stated that the linear combination $2 \cdot f(O) - f(H)$ of elemental balances: $f(H)$ for H and $f(O)$ for O is the property distinguishing between redox and non-redox electrolytic systems. Namely, $2 \cdot f(O) - f(H)$ is the linear combination of concentration balances for other components of a non-redox system, of any degree of complexity. It is also proved that $2 \cdot f(O) - f(H)$ is an independent equation when referred to a redox system, of any degree of complexity. The linear combination $2 \cdot f(O) - f(H)$ is a primary form, pr-GEB, of the Generalized Electron Balance (GEB), $2 \cdot f(O) - f(H) = pr$-GEB, named as the Approach II, and considered as the alternative for the Approach I to GEB, based on the "card game" principle. The equivalency of both approaches to GEB is also proved in this paper. The GEB, considered as a relatively new Law of Nature, is perceived as a turning point in the theory of electrolytic redox systems.

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1. Introduction

The main component of aqueous electrolytic systems is water. The species $X_i^{Z_i}$ present in such systems form hydrates, $X_i^{Z_i} \cdot n_i H_2O$, where $z_i = 0, \pm 1, \pm 2, \ldots$ is the charge of this species expressed in elementary charge units, $e = F/N_A$ (F – Faraday's constant, N_A – Avogadro's number), and $n_i \geq 0$ is the mean number of water particles attached to this species, whose concentration [mol/L] in this system is denoted as $[X_i^{Z_i}]$. In all further calculations, we will start with the number N_i of individual species, characterized by the notation $X_i^{Z_i}(N_i, n_i)$, for brevity. For example, CH_3COOH (N_6, n_6) denotes N_6 molecules of $CH_3COOH \cdot n_6 H_2O$; in this case, $i = 6$, and $z_6 = 0$.

The species of any electrolytic non-redox aqueous system are involved in charge and concentration balances: one charge balance

$$\sum_{i=1}^{p} z_i \cdot [X_i^{Z_i}] = 0 \tag{1}$$

(for p kinds of charged species) and k (≥ 1) concentration balances, referred to element(s) $X \neq H$, O or some "clusters" of elements involving X, named as "cores"; the term "core" is referred to clusters of atoms, involving elements $X \neq H$, O. Together, $k + 1$ balances are referred to non-redox systems.

Referring now to redox systems, one can state that, before 1992, the set of compatible balances for such systems has not been completed. Except charge and concentration balances, the balance referred to

(i) distribution of electrons between the species of one electron-active element in disproportionation or synproportionation reactions, or
(ii) transmission of electrons between the species of two or more electron-active elements involved in a common redox systems,

was needed. The principle of formulation of the desired, $k + 2$th balance, named first as electron prebalance, and later as the Generalized Electron Balance (GEB), has been devised by Michałowski (1992) and presented later in a number of works specified in [1].

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Notations

D	titrand (solution titrated)
T	titrant
V	volume [mL] of T
V_0	volume [mL] of D

From historical viewpoint, two equivalent approaches to GEB were applied [1]. The Approach I is based on a "card game" principle, with electron-active elements as "players", electron-non-active elements as "fans", and electrons as "money". The transmission of electrons occurs between different species formed by players, whereas such transmission does not occur between fans (the fans' accounts are intact). Another version of GEB is the Approach II, formulated on the basis of linear combination $2 \cdot f(O) - f(H)$ of elemental balances: $f(O)$ for O and $f(H)$ for H. GEB is perceived as a law of the matter conservation, as a relatively new Law of Nature [1,2].
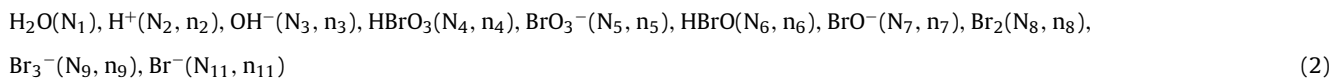
Referring to the elemental balances, one can put two simple questions: ($1°$) why the formulation of elemental balances for H and O was not practiced, and ($2°$) is it obligatory for any electrolytic system?

These questions seem to be reasonable, especially in context with the fact that water is, as a rule, the main carrier of H and O in aqueous solutions. This obvious fact was usually unnoticed in quantitative discussions on these systems, where elemental balances are commonly formulated for elements different from hydrogen and oxygen. In this context, we refer first to non-redox systems, where only acid–base equilibria occur. Then we consider more complex systems, where acid–base, complexation and precipitation reactions are involved. Subsequently we consider the most complex systems, where redox equilibria are accompanied by acid–base, complexation and precipitation reactions. In all instances, the closed systems, separated from the environment by diathermal walls, will be considered; it enables any processes to be carried out under isothermal conditions.

The $2 \cdot f(O) - f(H)$ will be combined (linear combination) with other concentration balances. This way, it will be proved that $2 \cdot f(O) - f(H)$ relating to a non-redox system is linearly dependent on the charge balance and other concentration balance(s) referred to this system. This way it will be proved that any non-redox system is described with charge and k concentration balances related to element(s) $X_i \neq$ H and O or cores – together $k+1$ balances. In other words, $2 \cdot f(O) - f(H)$ is not a new (independent) balance for any non-redox system. This property is valid for non-redox systems of any degree of complexity. The balance $2 \cdot f(O) - f(H)$ referred to a redox system is the equation linearly independent on other balances of this system; it is named as a *pr*imary form of the Generalized Electron Balance (GEB), and denoted as *pr*-GEB $= 2 \cdot f(O) - f(H)$. By a proper, linear combination of *pr*-GEB with other (charge and concentration) balances, one obtains the simpler (i.e., containing smaller number of the components involved) form of GEB. However, any of the linear combinations of *pr*-GEB with these balances has full properties of GEB, when applied for resolution of a redox system. This property is valid for any redox system, of any degree of complexity. Anyway, the GEB completes the set composed of charge balance and k concentration balances, necessary for quantitative description of redox systems. This way, any redox system is described with use of $k+2$ balances.

2. Approach I to GEB

The principle of formulation of GEB according to Approach I has been presented first time in [3], on an example of disproportionation (dismutation) of Br_2 molecules when introduced into aqueous media. In V mL of the solution obtained after introducing N_{10} molecules of Br_2 into N_{20} molecules of H_2O, we have the following species:

$$H_2O(N_1), H^+(N_2, n_2), OH^-(N_3, n_3), HBrO_3(N_4, n_4), BrO_3^-(N_5, n_5), HBrO(N_6, n_6), BrO^-(N_7, n_7), Br_2(N_8, n_8),$$

$$Br_3^-(N_9, n_9), Br^-(N_{11}, n_{11}) \tag{2}$$

In this system, the only player is Br_2, whose electrons are dissipated between different bromine species; H and O are not oxidized/reduced in this system and they are considered as fans. Denoting $Z_{Br} = 35$ – atomic number for Br (equal to the number of orbital electrons in bromine atom), we state that N_{10} molecules of Br_2 introduce $2Z_{Br}N_{10}$ bromine electrons. As a result of disproportionation, in the resulting solution we have, among others: N_4 entities of $HBrO_3 \cdot n_4 H_2O$ involving $(Z_{Br}-5)N_4$ bromine electrons, N_5 entities of $BrO_3^- \cdot n_5 H_2O$ involving $(Z_{Br}-5)N_5$ bromine electrons, N_6 entities of $HBrO \cdot n_6 H_2O$ involving $(Z_{Br}-1)N_6$ bromine electrons, N_7 entities of $BrO^- \cdot n_7 H_2O$ involving $(Z_{Br}-1)N_7$ bromine electrons, N_8 entities of Br_2 involving $2Z_{Br}N_{10}$ bromine electrons, N_9 entities of Br_3^- involving $(3Z_{Br}+1)N_9$ bromine electrons, and N_{11} entities of Br^- involving $(Z_{Br}+1)N_{11}$ bromine electrons. Balancing the bromine electrons, we have

$$(Z_{Br}-5)(N_4+N_5) + (Z_{Br}-1)(N_6+N_7) + 2Z_{Br}N_8 + (3Z_{Br}+1)N_9 + (Z_{Br}+1)N_{11} = 2Z_{Br}N_{10} \tag{3}$$

Applying the notations

$$[X_i^{Z_i}] \cdot V = 10^3 \cdot \frac{N_i}{N_A}, \quad \text{i.e. } N_i = 10^{-3} \cdot [X_i^{Z_i}] \cdot V \cdot N_A \quad \text{and} \quad C \cdot V = 10^3 \cdot \frac{N_{10}}{N_A}, \quad \text{i.e., } N_{10} = 10^{-3} \cdot C \cdot V \cdot N_A \tag{4}$$

in (3), we get the relation

$$(Z_{Br}-5)([HBrO_3] + [BrO_3^-]) + (Z_{Br}-1)([HBrO] + [BrO^-]) + 2Z_{Br}[Br_2] + (3Z_{Br}+1)[Br_3^-] + (Z_{Br}+1)[Br^-] = 2Z_{Br}C \tag{5}$$

related to C mol/L solution of Br_2 and expressed in terms of molar concentrations; N_A in (4) is the Avogardo's number.

In a synproportionation (comproportionation) reactions, there are electrons introduced by two (or more) substances formed by the same element, considered as a player. As an example, we consider a dynamic system, with Br as the player in a system obtained after addition of V mL of C mol/L $KBrO_3$ into V_0 mL of NaBr (C_0) + H_2SO_4 (C_1). We assume that V mL of the titrant is composed of N_{10} molecules of $KBrO_3$ and N_{20} molecules of H_2O, and V_0 mL of the titrand was composed N_{30} molecules of NaBr, N_{40} molecules of H_2SO_4 and N_{50} molecules