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GATES/GEB as the New Paradigm for Electrolytic Redox Systems

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Introduction

One of the most important achievements in formulation of electrolytic systems is the discovery of Generalized Electron Balance (GEB) [1], as an equation (unknown earlier in Science) completing the set of equations needed for thermodynamic solving electrolytic redox systems of any degree of complexity, i.e., equilibrium, metastable and kinetic systems, in mono-phase, two-phase, multiphase, and multi-solvent media. Redox and non-redox systems are resolved according to Generalized Approach to Electrolytic Systems (GATES) [2,3], formulated by Michałowski (1992); for redox systems, the acronym GATES/GEB is applied.

GATES is referred to aqueous, non-aqueous and mixed-solvent media A_s (s=1,...,S), with amphiprotic (co)solvent(s) involved [4]. In aqueous media, the species $X_i^{z_i}$ exist as hydrates $X_i^{z_i} \cdot n_{iW}$; $n_{iW} \geq 0$ is a mean number of water (W=H_2O) molecules attached to $X_i^{z_i}$. In the mixed-solvent media, formation of the mixed solvates $X_i^{z_i}\, n_{iA_1} \ldots n_{iA_s} \ldots n_{iA_S}$ is admitted, where $n_{iA_s} \geq 0$ is the mean numbers of A_s molecules attached to $X_i^{z_i}$ [5].

The GEB is recognized as the law of Nature [1], as the hidden connection of physicochemical laws, and as the breakthrough in thermodynamic theory of electrolytic redox systems. GEB was discovered by Michałowski: as the Approach I to GEB (1992), and as the Approach II to GEB (2005). In the Approach I to GEB, perceived according to 'card game' principle, electron-active elements are perceived as 'players', electron-non-active elements as 'fans', and electrons as 'money'; the knowledge of oxidation numbers is needed here. The Approach II introduces the balance $f_{12} = 2 \cdot f_2 - f_1$ as the combination of elemental balances: $f_1 = f(\mathrm{H})$ for Y_1 = H and $f_2 = f(\mathrm{O})$ for Y_2 = O. Charge balance (f_0 = ChB) and other elemental and core balances $f_k = f(Y_k)$ ($Y_k \neq$ H, O; k=3,...,K) are also considered within GATES. A core is considered as a cluster of different atoms with defined composition (expressed by chemical formula), structure and external charge, unchanged in the system in question.

Properties of the balances

In a non-redox system, the f_{12} is linearly dependent on the balances: $f_0, f_3, \ldots, f_K$, i.e., a non-redox system is formulated with use of K–1 independent balances $f_0, f_3, \ldots, f_K$. In a redox system, f_{12} is linearly independent on the balances $f_0, f_3, \ldots, f_K$, i.e., a redox system is formulated with use of K independent balances $f_0, f_{12}, f_3, \ldots, f_K$, The linear dependency or independency of f_{12} from $f_0, f_3, \ldots, f_K$ is then the general property distinguishing between non-redox and redox systems.

Other, general properties are also valid here. Among others, oxidation number (ON) is the derivative concept;

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application of controversial electronegativity (EN) concept, where an artificial/doubtful qualification of bonds is made, is thus avoided.

Formulation of GEB according to Approach II needs none prior knowledge of ONs of elements in all components forming a system and in all species present in the system. For a redox system with K–K* 'players', f_{12} is linearly independent on f_0, f_3,..., f_K, i.e., the redox system is described by K independent balances f_0, f_{12}, f_3,..., f_K. For a non-redox system (K*=K), f_{12} is linearly dependent on f_0, f_3,..., f_K, i.e., a non-redox system is described by K–1 independent balances f_0,f_3,...,f_K. Consequently, the linear combination $f_{12} + f_0 - \sum_{k=3}^{K^*} d_k \cdot f_k \Leftrightarrow \sum_{k=1}^{K^*} d_k \cdot f_k - f_0$ with d_k equal to the oxidation numbers of the related elements, is reducible to identity, 0 = 0. The linear combination $\sum_{k=1}^{K^*} d_k \cdot f_k - f_0$ applied to a redox system does not give the identity, also after further combination with K – K* balances for 'players'. The linear combination $\sum_{k=1}^{K^*} d_k \cdot f_k - f_0$ for a redox system is composed only of components and species, where 'players' are involved. These regularities are valid for electrolytic systems of any degree of complexity, with biological systems included *a* priori.

Redox titrations

Static and dynamic systems (aqueous media) were considered within GATES/GEB. Dynamic systems are realizable in simulated titrations, where V mL of titrant (T) is added into V_0 mL of titrand (D), at defined point of the titration; V is considered here as the steering variable. In general, D and T are composed of one or more solutes dissolved in water. One of solutes in D is analyte A, one of solutes in T is reagent B. The results of simulated redox titrations, realized with use of an iterative computer program, e.g. MATLAB [2]. Are plotted on the graphs: E = E(Φ) and pH = pH(Φ), where $\Phi = \frac{C \cdot V}{C_0 \cdot V_0}$ is the fraction titrated, C_0–concentration [mol/L] of A in D, C–concentration [mol/L] of B in T. Moreover, concentrations $[X_i^{z_i}]$ of the species $X_i^{z_i} \cdot n_{iW}$ are presented as dynamic speciation curves $\log[X_i^{z_i}] = \varphi_i(\phi)$. The plots related to different redox systems are presented in numerous articles, e.g. in [6-18], and other papers cited therein. Relatively simple redox systems are considered in [6,7].

Final comments

GATES provides the best thermodynamic tool, the entrance step towards better understanding the physicochemical concepts within biomedical chemistry. The knowledge of chemical processes is the basis for understanding the phenomena occurring in cells and in the body, perceived as the most complex electrolytic systems. This way, the interdisciplinary relationship of chemistry with physics, biology, pharmacy and medicine can (should) be highlighted. The description of the systems according to GATES (and GATES/ GEB in particular) principles is based on algebraic equations, not on the stoichiometry of reactions, practiced hitherto in scientific papers and book literature. The GATES proves to be the most useful on the preliminary stages of research programs. From the authors' viewpoint, stoichiometry is only a kind of 'dummy' [8,9,14,15,19]. A relic from the late eighteenth century.

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