

Formulation of Metastable Redox Systems According to GATES/GEB Principles. Simulated Ascorbinometric Titration of Ferricyanide

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Abstract

Simulated ascorbinometric titration of ferricyanide is considered from the viewpoint of thermodynamic instability of ferro- and ferricyanide species and their complexes, at different concentrations of H_2SO_4 . The results of calculations, made according to GATES/GEB principles, are illustrated graphically by $E = E(\Phi)$, $pH = pH(\Phi)$ relationships and speciation diagrams. This illustrates fundamental advantages offered by GATES/GEB in the field of simulation of metastable systems.

Keywords: Ascorbinometric Titration; Computer Simulation; Ferricyanide; GATES; GEB

Introduction

Ascorbinometric titrations (ascorbinometry) is the term introduced in analytical literature by Erdey [1], who used standardized solution of L-ascorbic acid ($C_6H_8O_6$, vitamin C) as titrant with reducing properties. The details of some methods of ascorbinometric titrations were reviewed in Erdey and Svehla monograph [2]. A newer, short review of potentiometric methods of vitamin C determination is presented in [3]. British Pharmacopoeia recommended the use of cerium(+4) ammonium sulfate [4] or iodine solution [5] as titrant; permanganate [2] and ferricyanide [6] solutions were also applied for this purpose. Ascorbinometric titration was also applied for determination of ferricyanide in different mixtures [7].

Earlier attempts to mathematical formulation of potentiometric titrations in redox systems, were based on stoichiometric notation; mathematical balancing and physicochemical knowledge were consistently neglected in quantitative considerations; this matter was raised/criticized by us in [8,9]. Many of that earlier papers issued later were – contrary to the factual state of things – unlawfully announced in the form of a validation, expressed in their titles by the term "general(ized)", totally inconsistent with the factual state of the matter. An example is here the work [10] addressed, among others, for ascorbinometric titration, with $I_2 + KI$ solution as titrant, and ascorbic acid as analyte. The stoichiometric leitmotif is seen also in more recent publications [11,12]

In this paper, the simulation will be realized according to Generalized Approach to Electrolytic Systems (GATES) principles [8,9,13-37]. The GATES formulated (1992) by Michałowski [14] for the needs of redox systems, is termed as GATES/GEB, where GEB is the Generalized Electron Balance, discovered by Michałowski, and introduced as two equivalent Approaches: I (1992) and II (2005) to GEB [13]. The GATES covers non-redox and redox systems, then $GATES/GEB \subset GATES$. The GEB, recognized as the Law

of Nature [13] is the hidden connection of physicochemical laws, and the breakthrough in thermodynamic theory of electrolytic redox systems. The GATES/GEB is the best possible thermodynamic approach to redox systems, of any degree of complexity, with use of all attainable thermodynamic knowledge involved in the related equilibrium data.

We consider hereinafter the simulated potentiometric titration of V_0 mL of $K_3Fe(CN)_6$ (C_0) + $MgCl_2$ (C_{01}) + KCl (C_{02}) + H_2SO_4 (C_{03}) + CO_2 (C_{04}) solution as titrant D with V mL of $C_6H_8O_6$ (C) + CO_2 (C_1) solution as titrant T [20]; $V_0 + V$ mL of D+T mixture is thus obtained, if the additivity of the volumes is pre-assumed/valid. The simulations are involved with thermodynamically possible decomposition of ferro- and ferricyanide complexes into constituent species, at different C_{03} values.

Preliminary data and notation

The paper provides an example of a dynamic electrolytic redox system realized according to titrimetric mode, where V mL of titrant T is added, up to a given point of the titration, into V_0 mL of titrand D, $T(V) \Leftrightarrow D(V_0)$. For modelling purposes, the titration is considered as the isothermal process realized in the closed system, separated from the environment by diathermal walls. The related system will be formulated according to the GATES principles, and resolved with use of iterative computer program MATLAB [14].

According to GATES/GEB principles, any species $X_i^{z_i}$ ($i = 1, \dots, I$) in an electrolytic system can be perceived in its natural form, i.e., as a hydrate $X_i^{z_i} n_{iW}$ in aqueous ($W=H_2O$) solution, where z_i ($z_i = 0, \pm 1, \pm 2, \dots$) is the external charge of $X_i^{z_i}$, expressed in terms of elementary charge unit $e = F/N_A$ (F – Faraday constant, N_A – Avogadro's number), and $n_{iW} \equiv n_{iW} \equiv n_{iW} H_2O$ (≥ 0) is the mean number of water (W) molecules attached to $X_i^{z_i}$. The known chemical formulas of $X_i^{z_i}$ provide the information necessary/sufficient to formulate the respective balances.

The terms: components and species are distinguished, for the balancing purposes. In the notation applied here, N_{0j} ($j=1,2,\dots,J$) be the number of molecules of a component of j -th kind, composing D and T in dynamic D+T system, whereby the D and T are composed separately from defined components, including water. The electrolytic system thus obtained involves N_1 molecules of H_2O and N_i species of i -th kind $X_i^{z_i}$, n_{iw} ($i=2,3,\dots,I$), denoted briefly as $X_i^{z_i}$ (N_i, n_i), where $n_i \equiv n_{iw} \equiv n_i H_2O$; then we have: H^+ (N_2, n_2), OH^- (N_3, n_3), ..., for ordering purposes. Molar concentration of the species $X_i^{z_i}$, n_{iw} in D+T system is denoted as $[X_i^{z_i}]$.

In the Approach I to GEB, regarded as 'card game', electron-active elements are perceived as 'players', electron-non-active elements as 'fans', and electrons as 'money' [13]; prior knowledge of oxidation numbers (ONs) is needed here. The Approach II to GEB, equivalent to the Approach I, introduces the balance $f_{12} = 2 \cdot f_2 - f_1$ as the linear combination of elemental balances: $f_1 = f(H)$ for $Y_1 = H$ and $f_2 = f(O)$ for $Y_2 = O$. For a redox system, f_{12} is the primary form of GEB, $f_{12} = 2 \cdot f_2 - f_1 = pr$ -GEB. Within GATES/GEB, the $f_{12} = 2 \cdot f(O) - f(H)$ is completed by charge balance ($f_0 = ChB$) and other, elemental and/or core balances $f_k = f(Y_k)$ ($Y_k \neq H, O$; $k=3,\dots,K$), i.e. $f_0, f_{12}, f_3, \dots, f_k$ is the complete set of K independent equations needed for the solution of a redox system. A core is a cluster of different atoms with defined composition (expressed by chemical formula), structure and external charge, unchanged in the system. Note that $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$ have different external charges. Therefore, the ferro- and ferricyanide species and their more complex forms (e.g., $H_3Fe(CN)_6^{-1}$, $MgFe(CN)_6^{-2}$; $HFe(CN)_6^{-2}$, $MgFe(CN)_6^{-1}$) have not a common core.

Formulation of the D+T system

As an example we consider the dynamic D+T system specified above. For calculation purposes, the following values are applied: $V_0 = 100$, $C_0 = 0.01$, $C = 0.1$, $C_{01} = C_{02} = 0.5$, $C_{04} = C_1 = 0.001$, $C_{03} = 0.01$ and 0.1 , i.e., two values for H_2SO_4 concentration (C_{03}) were assumed. This system can be described in details, in the following way.

V_0 mL of the titrand (D) containing N_{01} molecules of $K_3Fe(CN)_6$, N_{02} molecules of $MgCl_2 \cdot 6H_2O$, N_{03} molecules of KCl , N_{04} molecules of H_2SO_4 , N_{05} molecules of CO_2 , and N_{06} molecules of H_2O is titrated with V mL of the titrant T containing N_{07} molecules of $C_6H_8O_6$, N_{08} molecules of CO_2 and N_{09} molecules of H_2O . In the D+T system thus obtained, we have the following species:

H_2O (N_1), H^+ (N_2, n_2), OH^- (N_3, n_3), K^+ (N_4, n_4), HCN (N_5, n_5), CN^{-1} (N_6, n_6), H_2CO_3 (N_7, n_7), HCO_3^{-1} (N_8, n_8), CO_3^{-2} (N_9, n_9), $Fe(CN)_6^{-4}$ (N_{10}, n_{10}), $HFe(CN)_6^{-3}$ (N_{11}, n_{11}), $H_2Fe(CN)_6^{-2}$ (N_{12}, n_{12}), $H_3Fe(CN)_6^{-1}$ (N_{13}, n_{13}), $KFe(CN)_6^{-3}$ (N_{14}, n_{14}), $MgFe(CN)_6^{-2}$ (N_{15}, n_{15}); $Fe(CN)_6^{-3}$ (N_{16}, n_{16}), $HFe(CN)_6^{-2}$ (N_{17}, n_{17}), $KFe(CN)_6^{-2}$ (N_{18}, n_{18}), $MgFe(CN)_6^{-1}$ (N_{19}, n_{19}); Fe^{+2} (N_{20}, n_{20}), $FeOH^{+1}$ (N_{21}, n_{21}), $FeSO_4$ (N_{22}, n_{22}), Fe^{+3} (N_{23}, n_{23}), $FeOH^{+2}$ (N_{24}, n_{24}), $Fe(OH)_2^{+1}$ (N_{25}, n_{25}), $Fe_2(OH)_2^{+4}$ (N_{26}, n_{26}), $FeSO_4^{+1}$ (N_{27}, n_{27}), $Fe(SO_4)_2^{-1}$ (N_{28}, n_{28}), Mg^{+2} (N_{29}, n_{29}); $MgOH^{+1}$ (N_{30}, n_{30}), $MgSO_4$ (N_{31}, n_{31}), $C_6H_6O_6^{-2}$ (N_{32}, n_{32}), $C_6H_7O_6^{-1}$ (N_{33}, n_{33}), $C_6H_8O_6$ (N_{34}, n_{34}), $C_6H_6O_6$ (N_{35}, n_{35}), HSO_4^{-1} (N_{36}, n_{36}), SO_4^{-2} (N_{37}, n_{37}), Cl^{-1} (N_{38}, n_{38}). (1)

The components and species of the D+T system are interrelated

within charge and elemental/core balances:

$$f_0 = ChB$$

$$N_2 - N_3 + N_4 - N_6 - N_8 - 2N_9 - 4N_{10} - 3N_{11} - 2N_{12} - N_{13} - 3N_{14} - 2N_{15} - 3N_{16} - 2N_{17} - 2N_{18} - N_{19} + 2N_{20} + N_{21} + 3N_{23} + 2N_{24} + N_{25} + 4N_{26} + N_{27} - N_{28} + 2N_{29} + N_{30} - 2N_{32} - N_{33} - N_{36} - 2N_{37} - N_{38} = 0 \quad (2)$$

$$f_1 = f(H)$$

$$2N_1 + N_2(1 + 2n_2) + N_3(1 + 2n_3) + 2N_4n_4 + N_5(1 + 2n_5) + 2N_6n_6 + N_7(2 + 2n_7) + N_8(1 + 2n_8) + 2N_9n_9 + 2N_{10}n_{10} + N_{11}(1 + 2n_{11}) + N_{12}(2 + 2n_{12}) + N_{13}(3 + 2n_{13}) + 2N_{14}n_{14} + 2N_{15}n_{15} + 2N_{16}n_{16} + N_{17}(1 + 2n_{17}) + 2N_{18}n_{18} + 2N_{19}n_{19} + 2N_{20}n_{20} + N_{21}(1 + 2n_{21}) + 2N_{22}n_{22} + 2N_{23}n_{23} + N_{24}(1 + 2n_{24}) + N_{25}(2 + 2n_{25}) + N_{26}(2 + 2n_{26}) + 2N_{27}n_{27} + 2N_{28}n_{28} + 2N_{29}n_{29} + N_{30}(1 + 2n_{30}) + 2N_{31}n_{31} + N_{32}(6 + 2n_{32}) + N_{33}(7 + 2n_{33}) + N_{34}(8 + 2n_{34}) + N_{35}(6 + 2n_{35}) + N_{36}(1 + 2n_{36}) + 2N_{37}n_{37} + 2N_{38}n_{38} = 12N_{02} + 2N_{04} + 2N_{06} + 8N_{07} + 2N_{09}$$

$$f_2 = f(O)$$

$$N_1 + N_2n_2 + N_3(1 + n_3) + N_4n_4 + N_5n_5 + N_6n_6 + N_7(3 + n_7) + N_8(3 + n_8) + N_9(3 + n_9) + N_{10}n_{10} + N_{11}n_{11} + N_{12}n_{12} + N_{13}n_{13} + N_{14}n_{14} + N_{15}n_{15} + N_{16}n_{16} + N_{17}n_{17} + N_{18}n_{18} + N_{19}n_{19} + N_{20}n_{20} + N_{21}(1 + n_{21}) + N_{22}(4 + n_{22}) + N_{23}n_{23} + N_{24}(1 + n_{24}) + N_{25}(2 + n_{25}) + N_{26}(2 + n_{26}) + N_{27}(4 + n_{27}) + N_{28}(8 + n_{28}) + N_{29}n_{29} + N_{30}(1 + n_{30}) + N_{31}(4 + n_{31}) + N_{32}(6 + n_{32}) + N_{33}(6 + n_{33}) + N_{34}(6 + n_{34}) + N_{35}(6 + n_{35}) + N_{36}(4 + n_{36}) + N_{37}(4 + n_{37}) + N_{38}n_{38} = 6N_{02} + 4N_{04} + 2N_{05} + N_{06} + 6N_{07} + 2N_{08} + N_{09}$$

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

$$-N_2 + N_3 - N_5 + 4N_7 + 5N_8 + 6N_9 - N_{11} - 2N_{12} - 3N_{13} - N_{17} + N_{21} + 8N_{22} + N_{24} + 2N_{25} + 2N_{26} + 8N_{27} + 16N_{28} + N_{30} + 8N_{31} + 6N_{32} + 5N_{33} + 4N_{34} + 6N_{35} + 7N_{36} + 8N_{37} = 6N_{04} + 4N_{05} + 4N_{07} + 4N_{08} \quad (3)$$

$$-f_3 = -f(K)$$

$$3N_{01} + N_{03} = N_4 + N_{14} + N_{18} \quad (4)$$

$$-2f_4 = -2f(Mg)$$

$$2N_{02} = 2N_{15} + 2N_{19} + 2N_{29} + 2N_{30} + 2N_{31} \quad (5)$$

$$f_5 = f(Cl)$$

$$N_{38} = 2N_{02} + N_{03} \quad (6)$$

$$-4f_6 = -4f(CO_3)$$

$$4N_{05} + 4N_{08} = 4N_7 + 4N_8 + 4N_9 \quad (7)$$

$$-6f_7 = -6f(SO_4)$$

$$6N_{04} = 6N_{22} + 6N_{27} + 12N_{28} + 6N_{31} + 6N_{36} + 6N_{37} \quad (8)$$

$$f_8 = f(CN)$$

$$N_5 + N_6 + 6N_{10} + 6N_{11} + 6N_{12} + 6N_{13} + 6N_{14} + 6N_{15} + 6N_{16} + 6N_{17} + 6N_{18} + 6N_{19} = 6N_{01} \quad (9)$$

$$-2f_9 = -2f(Fe)$$

$$2N_{01} = 2N_{10} + 2N_{11} + 2N_{12} + 2N_{13} + 2N_{14} + 2N_{15} + 2N_{16} + 2N_{17} + 2N_{18} + 2N_{19} + 2N_{20} + 2N_{21} + 2N_{22} + 2N_{23} + 2N_{24} + 2N_{25} + 4N_{26} + 2N_{27} + 2N_{28} \quad (10)$$

$$-6f_{10} = -6f(C_6H_6O_6)$$

$$6N_{07} = 6N_{35} + 6N_{36} + 6N_{37} + 6N_{38} \quad (11)$$

The notation idea, similar to one suggested elsewhere is applied here. After addition of Equations (2) – (11) and cancellations, we get the linear combination

$$f_{12} + f_0 - f_3 - 2f_4 + f_5 - 4f_6 - 6f_7 + f_8 - 2f_9 - 6f_{10} \\ N_{16} + N_{17} + N_{18} + N_{19} + N_{23} + N_{24} + N_{25} + 2N_{26} + N_{27} + N_{28} - 2(N_{35} + N_{36} \\ + N_{37}) = N_{01} - 2N_{07} \quad (12)$$

Applying here the relations:

$$[X_1^{2+}](V_0 + V) = 10^3 \cdot \frac{N_1}{N_A}, C_0V_0 = 10^3 \cdot \frac{N_{01}}{N_A}, C_{01}V_0 = 10^3 \cdot \frac{N_{02}}{N_A}, \\ C_{02}V_0 = 10^3 \cdot \frac{N_{03}}{N_A}, C_{03}V_0 = 10^3 \cdot \frac{N_{04}}{N_A}, C_{04}V_0 = 10^3 \cdot \frac{N_{05}}{N_A}, \\ CV = 10^3 \cdot \frac{N_{07}}{N_A}, C_1V = 10^3 \cdot \frac{N_{08}}{N_A} \quad (13)$$

we obtain the equations:

$$F(1) = [\text{Fe}(\text{CN})_6^{-3}] + [\text{HFe}(\text{CN})_6^{-2}] + [\text{KFe}(\text{CN})_6^{-2}] + [\text{MgFe}(\text{CN})_6^{-1}] + [\text{Fe}^{+3}] \\ + [\text{FeOH}^{+2}] + [\text{Fe}(\text{OH})_2^{+1}] + 2[\text{Fe}_2(\text{OH})_2^{+4}] + [\text{FeSO}_4^{+1}] + [\text{Fe}(\text{SO}_4)_2^{-1}] - \\ 2([\text{C}_6\text{H}_6\text{O}_6^{-2}] + [\text{C}_6\text{H}_7\text{O}_6^{-1}] + [\text{C}_6\text{H}_8\text{O}_6]) - (C_0V_0 - 2CV)/(V_0 + V) = 0 \quad (12a)$$

$$F(2) = [\text{H}^{+1}] - [\text{OH}^{-1}] + [\text{K}^{+1}] - [\text{CN}^{-1}] - [\text{HCO}_3^{-1}] - 2[\text{CO}_3^{-2}] - \\ 4[\text{Fe}(\text{CN})_6^{-4}] - 3[\text{HFe}(\text{CN})_6^{-3}] - 2[\text{H}_2\text{Fe}(\text{CN})_6^{-2}] - [\text{H}_3\text{Fe}(\text{CN})_6^{-1}] - \\ 3[\text{KFe}(\text{CN})_6^{-3}] - 2[\text{MgFe}(\text{CN})_6^{-2}] - 3[\text{Fe}(\text{CN})_6^{-3}] - 2[\text{HFe}(\text{CN})_6^{-2}] \\ - 2[\text{KFe}(\text{CN})_6^{-2}] - [\text{MgFe}(\text{CN})_6^{-1}] + 2[\text{Fe}^{+2}] + [\text{FeOH}^{+1}] + 3[\text{Fe}^{+3}] + \\ 2[\text{FeOH}^{+2}] + [\text{Fe}(\text{OH})_2^{+1}] + 4[\text{Fe}_2(\text{OH})_2^{+4}] + [\text{FeSO}_4^{+1}] - [\text{Fe}(\text{SO}_4)_2^{-1}] + \\ 2[\text{Mg}^{+2}] + [\text{MgOH}^{+1}] - 2[\text{C}_6\text{H}_6\text{O}_6^{-2}] - [\text{C}_6\text{H}_7\text{O}_6^{-1}] - [\text{HSO}_4^{-1}] - 2[\text{SO}_4^{-2}] - \\ [\text{Cl}^{-1}] = 0 \quad (2a)$$

$$F(3) = [\text{K}^{+1}] + [\text{KFe}(\text{CN})_6^{-3}] + [\text{KFe}(\text{CN})_6^{-2}] - (3C_0V_0 + C_{02}V_0)/(V_0 + V) = 0 \quad (4a)$$

$$F(4) = [\text{Mg}^{+2}] + [\text{MgOH}^{+1}] + [\text{MgSO}_4] + [\text{MgFe}(\text{CN})_6^{-2}] + [\text{MgFe}(\text{CN})_6^{-1}] \\ - C_{01}V_0/(V_0 + V) = 0 \quad (5a)$$

$$F(5) = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^{-1}] + [\text{CO}_3^{-2}] - (C_{04}V_0 + C_1V)/(V_0 + V) = 0 \quad (7a)$$

$$F(6) = [\text{HSO}_4^{-1}] + [\text{SO}_4^{-2}] + [\text{FeSO}_4] + [\text{FeSO}_4^{+1}] + 2[\text{Fe}(\text{SO}_4)_2^{-1}] + \\ [\text{MgSO}_4] - C_{03}V_0/(V_0 + V) = 0 \quad (8a)$$

$$F(7) = [\text{HCN}] + [\text{CN}^{-1}] + 6[\text{Fe}(\text{CN})_6^{-4}] + 6[\text{HFe}(\text{CN})_6^{-3}] + 6[\text{H}_2\text{Fe}(\text{CN})_6^{-2}] \\ + 6[\text{H}_3\text{Fe}(\text{CN})_6^{-1}] + 6[\text{KFe}(\text{CN})_6^{-3}] + 6[\text{MgFe}(\text{CN})_6^{-2}] + 6[\text{Fe}(\text{CN})_6^{-3}] + \\ 6[\text{HFe}(\text{CN})_6^{-2}] + 6[\text{KFe}(\text{CN})_6^{-2}] + 6[\text{MgFe}(\text{CN})_6^{-1}] - 6C_0V_0/(V_0 + V) = 0 \quad (9a)$$

$$F(8) = [\text{Fe}(\text{CN})_6^{-4}] + [\text{HFe}(\text{CN})_6^{-3}] + [\text{H}_2\text{Fe}(\text{CN})_6^{-2}] + [\text{H}_3\text{Fe}(\text{CN})_6^{-1}] + \\ [\text{KFe}(\text{CN})_6^{-3}] + [\text{MgFe}(\text{CN})_6^{-2}] + [\text{Fe}(\text{CN})_6^{-3}] + [\text{HFe}(\text{CN})_6^{-2}] + \\ [\text{KFe}(\text{CN})_6^{-2}] + [\text{MgFe}(\text{CN})_6^{-1}] + [\text{Fe}^{+2}] + [\text{FeOH}^{+1}] + [\text{FeSO}_4] + [\text{Fe}^{+3}] \\ + [\text{FeOH}^{+2}] + [\text{Fe}(\text{OH})_2^{+1}] + 2[\text{Fe}_2(\text{OH})_2^{+4}] + [\text{FeSO}_4^{+1}] + [\text{Fe}(\text{SO}_4)_2^{-1}] - \\ C_0V_0/(V_0 + V) = 0 \quad (10a)$$

$$F(9) = [\text{C}_6\text{H}_6\text{O}_6^{-2}] + [\text{C}_6\text{H}_7\text{O}_6^{-1}] + [\text{C}_6\text{H}_8\text{O}_6] + [\text{C}_6\text{H}_6\text{O}_6] - CV/(V_0 + V) = 0 \quad (11a)$$

The relation $[\text{Cl}^{-1}] = (2C_{01} + C_{02})V_0/(V_0 + V)$ obtained from the balance (6), is an equality, not equation; it can enter immediately the charge balance (2a).

The number of independent equations: $F(1), \dots, F(9)$ is equal to the number of variables, specified as follows:

$$x(1) = E, x(2) = \text{pH}, x(3) = \text{pFe3CN6}, x(4) = \text{pC6H6O6}, x(5) = \text{pSO4}, \\ x(6) = \text{pMg}, x(7) = \text{pK}, x(8) = \text{pH2CO3}, x(9) = \text{pHCN}, \\ \text{where:}$$

$$\text{pFe3CN6} = -\log[\text{Fe}(\text{CN})_6^{-3}], \text{pC6H6O6} = -\log[\text{C}_6\text{H}_6\text{O}_6], \\ \text{pSO4} = -\log[\text{SO}_4^{-2}], \text{pMg} = -\log[\text{Mg}^{+2}], \text{pK} = -\log[\text{K}^{+1}], \\ \text{pH}_2\text{CO}_3 = -\log[\text{H}_2\text{CO}_3].$$

The set of concentrations and relations for equilibrium constants, written in terms of the notation required/tolerated in MATLAB, is as follows:

$$\text{H} = 10^{-(\text{pH})}, \text{pKw} = 14, \text{Kw} = 10^{-(14)}, \text{OH} = \text{Kw}/\text{H}, \\ \text{H2CO3} = 10^{-(\text{pH2CO3})}, \text{HCO3} = 10^{-(6.3)} \cdot \text{H2CO3}/\text{H}, \\ \text{CO3} = 10^{-(10.1)} \cdot \text{HCO3}/\text{H}, \text{HCN} = 10^{-(\text{pHCN})}, \\ \text{CN} = 10^{-(9.2)} \cdot \text{HCN}/\text{H}, \text{SO4} = 10^{-(\text{pSO4})}, \\ \text{HSO4} = 10^{1.8} \cdot \text{H} \cdot \text{SO4}, \text{Fe3CN6} = 10^{-(\text{pFe3CN6})}, \\ \text{Fe3} = 10^{(-43.6)} \cdot \text{Fe3CN6} \cdot \text{CN}^{(-6)}, A = 16.9, \\ \text{Fe2} = \text{Fe3} \cdot 10^{(A \cdot (0.771 - E))}, \text{Fe2CN6} = 10^{35.4} \cdot \text{Fe2} \cdot \text{CN}^{(6)}, \\ \text{Fe2OH} = 10^{(4.5)} \cdot \text{Fe2} \cdot \text{OH}, \text{Fe3OH} = 10^{(11.0)} \cdot \text{Fe3} \cdot \text{OH}, \\ \text{Fe3OH2} = 10^{(21.7)} \cdot \text{Fe3} \cdot \text{OH}, \text{Fe32OH2} = 10^{(25.1)} \cdot \text{Fe3}^2 \cdot \text{OH}^2, \\ \text{Fe2SO4} = 10^{(2.3)} \cdot \text{Fe2} \cdot \text{SO4}, \text{Fe3SO4} = 10^{(4.18)} \cdot \text{Fe3} \cdot \text{SO4}, \\ \text{Fe3SO42} = 10^{(7.4)} \cdot \text{Fe3} \cdot \text{SO4}^2, \text{HFe2CN6} = 10^{(4.28)} \cdot \text{H} \cdot \text{Fe2CN6}, \\ \text{H2Fe2CN6} = 10^{(6.58)} \cdot \text{H}^2 \cdot \text{Fe2CN6}, \\ \text{H3Fe2CN6} = 10^{(6.58)} \cdot \text{H}^3 \cdot \text{Fe2CN6}, \text{HFe3CN6} = 10^{(1.0)} \cdot \text{H} \cdot \text{Fe3CN6}, \\ \text{Mg} = 10^{-(\text{pMg})}, \text{K} = 10^{-(\text{pK})}, \text{MgSO4} = 10^{(2.25)} \cdot \text{Mg} \cdot \text{SO4}, \text{Mg-} \\ \text{Fe2CN6} = 10^{(3.81)} \cdot \text{Mg} \cdot \text{Fe2CN6}, \text{MgFe3CN6} = 10^{(2.79)} \cdot \text{Mg} \cdot \\ \text{Fe3CN6}, \text{KFe2CN6} = 10^{(2.3)} \cdot \text{K} \cdot \text{Fe2CN6}, \text{KFe3CN6} = 10^{(1.4)} \cdot \text{K} \cdot \\ \text{Fe3CN6}, \\ \text{C6H6O6} = 10^{-(\text{pC6H6O6})}, \text{C6H8O6} = \text{C6H6O6} \cdot 10^{(-2 \cdot A \cdot (E - \\ 0.39) - 2 \cdot \text{pH})}, \text{C6H7O6} = \text{C6H8O6} \cdot 10^{(\text{pH} - 4.21)}, \\ \text{C6H6O6R} = \text{C6H8O6} \cdot 10^{(2 \cdot \text{pH} - 15.78)}, \\ \text{where C6H6O6R} = [\text{C}_6\text{H}_6\text{O}_6^{-2}].$$

Calculation procedure

The calculation procedure is realized according to iterative computer program MATLAB, analogous to that applied in [21]. It consists of minimizing the real, objective function, presented as the sum of squares (SS)

$$\text{SS} = F(1)^2 + F(2)^2 + F(3)^2 + F(4)^2 + F(5)^2 + F(6)^2 + F(7)^2 \\ + F(8)^2 + F(9)^2 \quad (14)$$

where $F(1), \dots, F(9)$ are defined by Equations: (12a), (2a), (4a), (5a), (7a), (8a), (9a), (10a), (11a). The optimization includes finding the best available values of the variables $x(1), \dots, x(9)$ for different V -values, considered as the current parameter of the D+T system, at defined point of the titration. On this basis, E , pH and concentrations of all species of the system are calculated at successive V -values. The V -values are recalculated on the fraction titrated [8,13,14,15,32] values

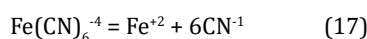
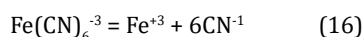
$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \quad (15)$$

Specification of the problem

In GATES/GEB, as the thermodynamic approach, a titration is considered as a quasistatic process, where equilibration time is not involved as variable. Therefore, the following options were applied:

- EQUI: Equilibrium option, all reaction paths, possible from thermodynamic viewpoint, are admitted;
- META: Metastable option, the indicated reaction paths, possible from thermodynamic viewpoint, are forbidden;

Dissociation of ferricyanide and ferrocyanide ions:



in simple and more complex species is admitted as: (a) possible in EQUI option, or (b) impossible in META option. Other dissociations, e.g. $\text{MgFe}(\text{CN})_6^{-1} = \text{Mg}^{+2} + \text{Fe}(\text{CN})_6^{-3}$, $\text{MgFe}(\text{CN})_6^{-2} = \text{Mg}^{+2} + \text{Fe}(\text{CN})_6^{-4}$, are possible in both options.

The EQUI and META options were realized at two C_{03} values for H_2SO_4 , and other data specified above, i.e., $V_0 = 100$, $C_0 = 0.01$, $C = 0.1$, $C_{01} = C_{02} = 0.5$, $C_{04} = C_1 = 0.001$. The results of calculations are presented graphically as functions $E = E(\Phi)$ and $\text{pH} = \text{pH}(\Phi)$ of the fraction titrated (Equation 15), and $\log [X_i^{Z_i}] = \varphi_i(\Phi)$, for speciation curves; the E-values [V] are expressed in SHE scale.

Graphical Presentation and Discussion

EQUI option, at $C_{03} = 0.01$.

The results are presented in Figures 1a – 1e, and in Table 1.

Table 1: The E and pH at Φ values close to 0.2 and 0.5, see Figures 1a,b.

	E	pH		E	pH
0,180	0,6456	3,543	0,480	0,2832	4,266
0,185	0,6350	3,571	0,485	0,2754	4,266
0,190	0,6193	3,614	0,490	0,2647	4,266
0,195	0,5891	3,697	0,495	0,2474	4,265
0,200	0,4920	3,967	0,500	0,2198	4,265
0,205	0,4516	4,077	0,505	0,2044	4,265
0,210	0,4356	4,119	0,510	0,1970	4,264
0,215	0,4254	4,145	0,515	0,1922	4,264
0,220	0,4179	4,163	0,520	0,1887	4,264

META option, at $C_{03} = 0.01$.

The results of calculations are presented in Figures 2a – 2d.

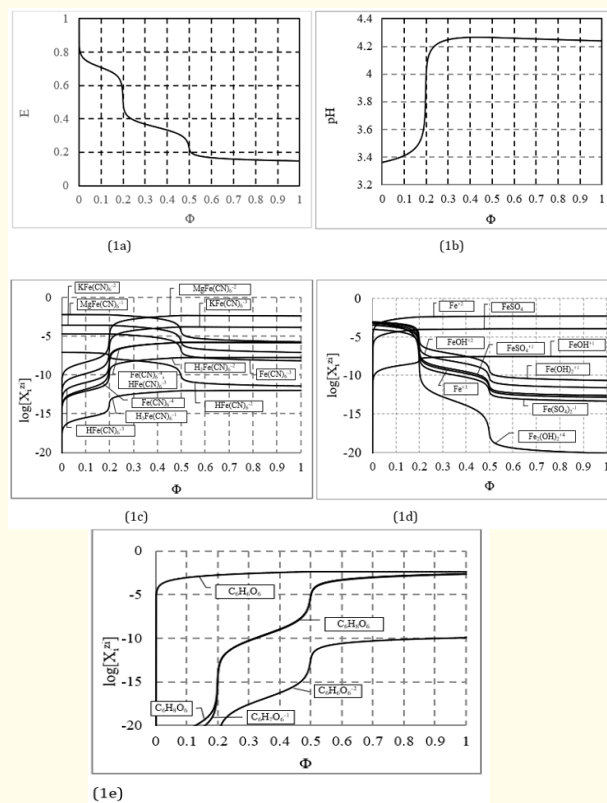


Figure 1: The (1a) $E = F(\Phi)$, (1b) $\text{pH} = \text{pH}(\Phi)$ and speciation curves for: (1c) ferro- and ferricyanide species, (1d) other iron species, (1e) ascorbate species, obtained for EQUI at $C_{03} = 0.01$.

Figure 2: The (2a) $E = F(\Phi)$, (2b) $\text{pH} = \text{pH}(\Phi)$ and speciation curves for: (2c) ferro- and ferricyanide species, (2d) ascorbate species, obtained for META at $C_{03} = 0.01$.

EQUI option, at $C_{03} = 0.1$.

The results of calculations are presented in Figures 3a – 3e.

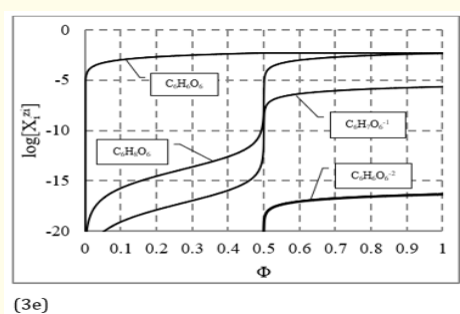


Figure 3: The (3a) $E = F(\Phi)$, (3b) $pH = pH(\Phi)$ and speciation curves for: (3c) ferro- and ferricyanide species, (3d) other iron species, (3e) ascorbate species, obtained for EQUI at $C_{03} = 0.1$.

META option, at $C_{03} = 0.1$.

The results of calculations are presented in Figures 4a – 4d.

According to the stoichiometric notation, when taking into account only the basic forms of the relevant species, we have the half-reactions: $Fe(CN)_6^{-3} + e^{-1} = Fe(CN)_6^{-4}$, $C_6H_8O_6 = C_6H_6O_6 + 2H^{+1} + 2e^{-1}$ and the resulting summary reaction



$$\frac{2}{C_0 \cdot V_0} \quad \frac{1}{C_{eq} \cdot V_{eq}}$$

From the resulting proportion we find the fraction titrated (Equation 15) value

$$\Phi_{eq} = \frac{C_{eq} \cdot V_{eq}}{C_0 \cdot V_0} = 0.5 \quad (19)$$

related to equivalent volume V_{eq} . Analogous dependence we find

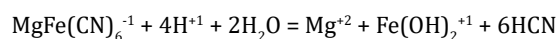
Figure 4: The (4a) $E = F(\Phi)$, (4b) $pH = pH(\Phi)$ and speciation curves for: (4c) ferro- and ferricyanide species, (4d) ascorbate species, obtained for META at $C_{03} = 0.1$.

for a reaction involving dominant ferri- and ferrocyanide species, $2MgFe(CN)_6^{-3} + C_6H_8O_6 = 2MgFe(CN)_6^{-4} + C_6H_6O_6 + 2H^{+1}$. At $V = V_{eq} = 0.5C_0V_0/C$, the related part of Equation (12a) is zeroing.

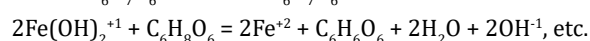
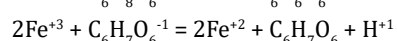
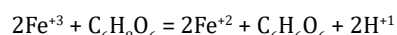
The $\Phi_{eq} = 0.5$ value is marked, more or less clearly, on the $E = E(\Phi)$ curves (Figures 1a, 2a, 3a, 4a), as well as on some $pH = pH(\Phi)$ curves (Figures 2b, 3b, 4b). Near $\Phi_{eq} = 0.5$, the pH ranges are narrow there, comparable with a maximum precision ± 0.001 of pH measurements. This effect is involved with the dynamic buffer capacity value [35,38]. In addition, these ranges occur at low pH values, where the characteristics of glass electrodes are nonlinear.

At the beginning of the titration, the $Fe(CN)_6^{-3}$ ions are bound mainly as $MgFe(CN)_6^{-1}$ (Figure 1c). Relatively high concentrations of other Fe(+3) species (Figure 1d) indicate that the dissociation (16) occurs in a significant degree.

In acidic (H_2SO_4) medium, CN^{-1} forms HCN, $CN^{-1} + H^{+1} = HCN$. At the beginning, the predominating form of Fe(+3) is $Fe(OH)_2^{+1}$. Therefore, the dominant reaction in this range, can be written as follows



where a part of protons (from H_2SO_4) is used. At the same time, redox reactions of $C_6H_8O_6$ and $C_6H_7O_6^{-1}$ (Figure 1e) with different Fe(+3) species (Figure 1d) occur, e.g.,



The resultant effects are the changes in E and pH values at the vicinity of $\Phi = 0.2$, shown in Figures 1a,b.

Conclusion

Among electrolytic redox systems, a significant group are metastable systems in which certain reaction paths, which can be implemented from a thermodynamic point of view, are available after providing the activation energy to the relevant components of the system. Crossing these barriers causes the formation of other, new reaction products, which essentially causes changes of potential E and pH, measured during potentiometric titration.

In the potentiometric titration, specific energy barriers may relate to the dissociation of particular components under given conditions of analysis. In the example considered here, the thermodynamically possible dissociation of $\text{Fe}(\text{CN})_6^{-3}$ and $\text{Fe}(\text{CN})_6^{-4}$ ions (Equations 16 and 17) and their complexes is attributed to the effect of H_2SO_4 in the titrand D titrated with ascorbic acid solution.

To demonstrate the metastable state of the indicated ions and their complexes, the simulated calculations were used in which the (actual) metastable state (META) of this system was compared with the thermodynamically possible equilibrium state (EQUI). These calculations were carried out for two values of H_2SO_4 concentration. The calculation results were demonstrated on the E = F(Φ) and pH = pH(Φ) dependences, and the speciation curves.

The simulation realized within GATES/GEB, with use of an iterative computer program, e.g. MATLAB, provides quite a new quality in knowledge gaining from attainable and pre-selected physicochemical data. It enables to follow the details of the process and gain the knowledge incomparably better than one offered hitherto by the well-known Pourbaix diagrams. The GATES avoids the inferences based on fragile/rachitic chemical reaction notation, involving only some of the species existing in the system. From the GATES viewpoint, the 'stoichiometry' can be perceived only as a mnemonic term.

Reactions related to the formation of gaseous products, e.g. O_2 , with limited solubility in the aquatic environment, require volumetric work, associated with formation of gas bubbles with a diameter exceeding an appropriate, critical value. In many systems, the work associated with formation of such bubbles is relatively large, and therefore such a process does not take place; then we have a metastable system. For example, the reaction $4\text{MnO}_4^{-1} + 2\text{H}_2\text{O} = 4\text{MnO}_2 + 3\text{O}_2 + 4\text{OH}^{-1}$ is thermodynamically possible, at room temperature. The high activation barrier associated with the volumetric work required to form O_2 bubbles causes that the solution obtained after introducing solid KMnO_4 into water is in a metastable state, even at boiling point of the solution [13].

In some other cases, it is possible to release gaseous products of limited solubility in water. For example, the reaction $2\text{MnO}_4^{-1} + 5\text{H}_2\text{C}_2\text{O}_4 + 6\text{H}^{+1} = 2\text{Mn}^{+2} + 10\text{CO}_2 + 8\text{H}_2\text{O}$ is very slow at room temperature, while it occurs effectively at elevated (60 – 70°C) temperatures; heating the reaction medium provides here the energy needed for transition of the activation barrier. Note that the physi-

cochemical data in the relevant tables of equilibrium constants were determined, as a rule, at temperatures approx. 20°C.

One of the first spectacular successes of GATES/GEB was the modelling of D+T system with $\text{KIO}_3 + \text{HCl} + \text{H}_2\text{SeO}_3 + \text{HgCl}_2$ solution as D titrated with ascorbic acid solution as T, presented in [14,23,37]. KIO_3 is the analyte A, $\text{C}_6\text{H}_8\text{O}_6$ is the reagent B. In simulated calculations, two options were applied.

In the first option, considered in three elements: I, C and Cl were considered as electron-active elements (players). In the second option, Se and Hg were also admitted as 'players'; together, five(!) electron-active elements: I, C, Cl, Se and Hg were assumed in the model applied in the system with 51 species involved in 7 independent balances and 40 independent equilibrium constants. The results of our simulations were presented in [14,23,32,37]. The results of simulated calculations were compared with the results of experimental titrations, presented in the paper [40]. The very interesting details related to this system are collected in [14].

Redox reactions involved with the proton transfer, are characterized by specific kinetics. An interesting example is the D+T system with $\text{As}_2\text{O}_3 + \text{NaOH} + \text{H}_2\text{SO}_4 +$ malonic acid ($\text{CH}_2\text{C}_2\text{O}_4\text{H}_2$) as D and $\text{I}_2 + \text{KI}$ solution as T [33]; malonic acid was applied there as the buffer-forming agent, with pH_0 ca. 6, at the start for the pH-titration. The pH = pH(V) curve thus obtained consisted of two rectilinear segments intersecting at the equivalence volume (V_{eq}). This way, a new analytical method was suggested. The more profound inspection of this interesting system, discussed also in the papers [23], indicated a rapid reaction of iodine with arsenite and a slow (kinetic) reaction of iodine with malonate.

The GATES was also applied for simulation of phenomena that occur in non-redox non-equilibrium two-phase systems, especially those involved with struvite and dolomite [17]. A four-stage process in dynamic two-phase redox system was considered in [25]. Simulation of two-phase dynamic liquid-liquid extraction system was exemplified in [36]. The papers [15] appears unnoticed earlier fact of non-monotonic course of pH vs. Φ relationship, stated also for other D+T redox systems [32].

Redox systems are the most important and most complex electrolytic systems. The transfer of electrons is usually accompanied by other (acid-base, complexation and precipitation) reactions. The complexity of redox systems is expressed by the number of equilibrium constants and by diversity of these constants involved with the system considered: acid-base dissociation constants, stability constants of complexes, solubility products, standard potentials, partition constants in liquid-liquid extraction systems, etc. The power of the GATES/GEB lies in its simplicity.

However, as hitherto, the GATES/GEB is not widely known to the scientific community, where the inferences based on chemical reaction notations and stoichiometry are still in common use. The importance of redox systems in chemistry is unquestionable. In this respect, a slight number of papers of other authors testifies unambiguously that the GATES/GEB is still unknown or incom-

prehensible for chemists, after 27 years passed after its discovery. Then the main purpose of the present paper is to familiarise it to a wider community. It was also indicated, in a simple mathematical manner (see e.g. [13] the fundamental criterion distinguishing between non-redox and redox systems. Contrary to appearances, this criterion, expressed by the linear combination $2 \cdot f(O) - f(H)$, is immediately associated with hydrogen (H) and oxygen (O), not(!) with free electrons in an electrolytic system [25].

The GATES/GEB is perceived as the unrivalled tool applicable, among others: (a) to mathematical modelling of thermodynamic behavior of redox systems, (b) in choice of optimal *a priori* conditions of chemical analyses, and (c) in gaining chemical information invisible in real experiments, in general. All the inferences made within GATES/GEB are based on firm, algebraic foundations. The approach proposed allows to understand far better all physicochemical phenomena occurring in the system in question and improve some methods of analysis. All the facts testify very well about the potency of simulated calculations made, according to GATES, with all attainable and pre-selected physicochemical knowledge involved. Possibilities of GATES/GEB are far greater than the actual physicochemical knowledge related to electrolytic redox systems is offered. Summarizing, GATES and GATES/GEB in particular, provides a new, reliable tool, thanks to which it will be possible, in the immediate future, a renaissance of interest in this – so important, after all! – field of fundamental research.

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