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Application of GATES and MATLAB for Resolution of Equilibrium, Metastable and Non-Equilibrium Electrolytic Systems

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1. Introduction

The Generalized Approach To Electrolytic Systems (GATES) (Michałowski, 2001, 2010) provides the possibility of thermodynamic description of equilibrium and metastable, redox and non-redox, mono-, two- and three-phase systems, with the possibility of all attainable/pre-selected physicochemical knowledge to be involved, with none simplifying assumptions done for calculation purposes, where different types of reactions occur in batch or dynamic systems, of any degree of complexity. The Generalized Electron Balance (GEB) concept, devised and formulated by Michałowski (1992), and obligatory for description of redox systems, is fully compatible with charge and concentration balances, and relations for the corresponding equilibrium constants. Up to 1992, the generalized electron balance (GEB) concept was the lacking segment needed to formulate the compatible set of algebraic balances referred to redox systems. The GEB is also applicable for the systems where radical species are formed. Shortly after GEB formulation, the GATES involving redox systems of any degree of complexity, was elaborated.

In this chapter, some examples of complex redox systems, where all types of elementary chemical reactions proceed simultaneously and/or sequentially, are presented. In all instances, one can follow measurable quantities (potential E , pH) in dynamic and static processes and gain the information about details not measurable in real experiments; it particularly refers to dynamic speciation. In the calculations made according to iterative computer programs, e.g., MATLAB, all physicochemical knowledge can be involved and different “variations on the subject” are also possible; it particularly refers to metastable and non-equilibrium systems. The Generalized Equivalent Mass (GEM) concept, also devised (1979) by Michałowski (Michałowski et al., 2010), has been suggested, with none relevance to a chemical reaction notation. Within GATES, the chemical reaction notation is only the basis to formulate the expression for the related equilibrium constant.

2. GEB

In order to formulate GEB for a particular redox system, two equivalent approaches were suggested by Michałowski. The first approach (Michałowski, 1994; Michałowski and Lesiak,

1994a,b) is based on the principle of a “common pool” of electrons, introduced by different species containing the electron-active elements participating redox equilibria. The disproportionation reaction is a kind of dissipation of electrons between the species formed by dissipating element, whereas the transfer of electrons between two (or more) interacting elements in a redox system resembles a “card game”, with active elements as gamblers, electrons - as money, and non-active elements - as fans.

The second approach (Michałowski, 2010) results from juxtaposition of elemental balances for hydrogen (H) and oxygen (O). For redox systems, the balance thus obtained is independent on charge and concentration balances, whereas the related balance, when referred to non-redox systems, is the linear combination of charge and concentration balances, i.e. it is not a new, independent balance (Fig. 1). Any non-redox system is thus described only by the set of charge and s concentration balances, together $s+1$ linearly independent balances. Any redox system is described with use of charge, electron (GEB) and s concentration balances, together $s+2$ linearly independent balances. Charge balance results from balance of protons in nuclei and orbital electrons of all elements in all species forming the electrolytic system considered.

For redox systems, the balance obtained according to the second approach can be transformed (Michałowski, 2010) into the form ascribed to the first approach. In the second approach, we are not forced to calculate oxidation degrees of elements in particular species; it is an advantageous occurrence, of capital importance for the systems containing complex organic compounds, their ions and/or radicals.

The principles of minimizing (zeroing) procedure, realized within GATES according to iterative computer program, are exemplified e.g., in (Michałowski, 1994; Michałowski and Lesiak, 1994a).

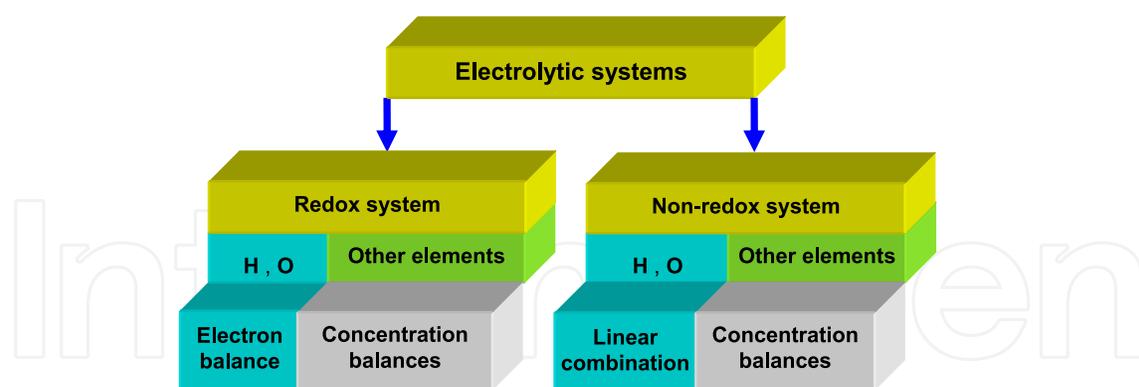


Fig. 1. The place of electron balance (GEB) within elemental balances.

3. General characteristics of electrolytic systems

Electrolytic systems can be considered from thermodynamic or kinetic viewpoints. The thermodynamic approach can be applied to equilibrium or metastable systems. In equilibrium systems, all reaction paths are accessible, whereas in metastable systems at least one of the reaction paths, attainable (virtually) from equilibrium viewpoint, is

inaccessible, i.e. the activation barriers for some reaction paths are not crossed, and the resulting reactions cannot proceed, under defined conditions. It particularly refers to aqueous electrolytic systems, where less soluble gaseous species, such as H_2 or O_2 , can virtually be formed, provided that this process is not hampered by obstacles of different nature. However, formation of the presupposed gas bubbles in the related solution, needs a relatively great expenditure of volumetric work, $\Delta L = -\int p \cdot dV$, made against the surrounding solution, by gas molecules forming the bubble. The ΔL value can be recalculated on an overvoltage $\Delta U = \Delta L/q$, where q is the charge consumed/released in the (virtual) reduction/oxidation process. Owing to the fact that the particular bubble assumes a macroscopic dimension, ΔL and then ΔU values are high. Particularly, ΔU referred to the (presupposed) formation of O_2 , cannot be covered by the oxidation potential of MnO_4^{-1} in aqueous medium and the (virtual) reaction $4MnO_4^{-1} + 4H^{+1} = 4MnO_2 + 3O_2 + 2H_2O$ does not occur, even at elevated temperatures. Another kind of obstacles resulted from formation of a hydroxide/oxide layer on surface of a metal (e.g., Mg, Al) introduced into pure water; these layers protect further dissolution of the metal and formation of H_2 .

One can distinguish static (batch) and dynamic electrolytic systems, resolvable within GATES. The dynamic process, most commonly applied in laboratory practice, is the titration, where titrant (T) is added into titrand (D), and the D+T system is thus formed. In D+T systems considered in chemical analysis, different (acid-base, redox, complexation or/and precipitation, extended on two- and three-phase (liquid-liquid extraction systems) types of reactions may occur simultaneously and/or sequentially and, moreover, a particular type of a reaction, e.g., complexation, can be exemplified by different representatives, e.g., different ligands.

Modelling the electrolytic systems consists of several interacting steps, indicated in Fig. 2. The collected preliminary data are of qualitative and quantitative nature. The qualitative aspect refers to specification of particular components (species), whereas quantitative aspect relates to equilibrium constants, involving particular species of the system. Later on, only the steps involved with calculations, data handling and knowledge gaining will be discussed.

4. Rules of conservation

In chemical systems, one can refer to different rules of conservation, due to elements, protons, electrons and external charges of species – particularly the species entering the electrolytic systems, where none nuclear transformations of elements occur. Some rules of conservation are interrelated, and this fact is referred to systems of any degree of complexity. This way, the problem of interdependency of the balances arises. Starting from the rules of conservation viewpoint, it is assumed, that any electrolytic system, composed of condensed (liquid, liquid+solid, liquid1+liquid2, or liquid1+liquid2+solid) phases (Michałowski and Lesiak, 1994a) is separated from its surroundings by diathermal walls, that enable any process in the closed system to proceed under isothermal conditions. In such systems, the mass transport can occur only between the phases consisting such a system. In thermodynamic considerations of dynamic electrolytic systems it is also assumed that all the processes occur in *quasistatic* manner.

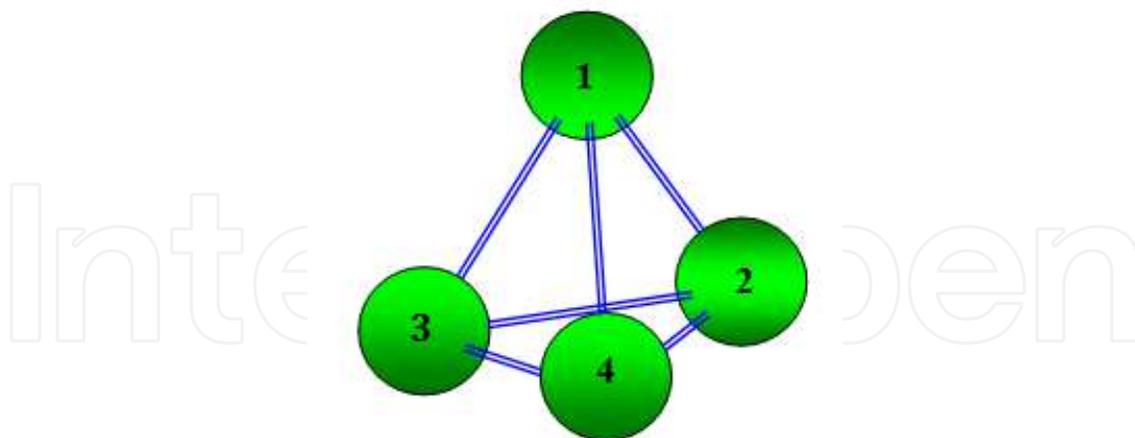


Fig. 2. Steps of modelling any electrolytic system: 1 - Collection of preliminary data; 2 - Preparation of computer program; 3 - Calculations and data handling; 4 - Gaining of knowledge.

As were stated above, the linear combination of elemental balances for hydrogen (H) and oxygen (O), referred to redox systems in aqueous media, provides the balance equivalent to GEB, in its primary form. In formulation of the balances, formation of hydrated forms $X_i^{z_i} \times n_i \text{H}_2\text{O}$ ($n_i \geq 0$) of ionic ($z_i \neq 0$) and/or nonionic ($z_i = 0$) species $X_i^{z_i}$ is admitted in considerations. The GEB, referred to a redox system, is fully compatible with other (charge and concentration) balances related to this system and is linearly independent from that balances.

5. Formulation of GEB

5.1 Batch redox systems

5.1.1 Fenton reagent

The Fenton reagent is usually obtained by mixing FeSO_4 and H_2O_2 solutions. In order to describe this redox system quantitatively, let us consider the monophasic system (solution) of volume V_0 [L], composed of N_{01} molecules of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, N_{02} molecules of H_2O_2 and N_{0W} molecules of H_2O introduced with H_2O_2 solution (e.g., perhydrol), and N_W molecules of H_2O as the solvent. The solution: H_2O (N_1), H^{+1} (N_2, n_2), OH^{-1} (N_3, n_3), OH (N_4, n_4), H_2O_2 (N_5, n_5), HO_2^{-1} (N_6, n_6), HO_2 (N_7, n_7), O_2^{-1} (N_8, n_8), O_2 (N_9, n_9), Fe^{+2} (N_{10}, n_{10}), FeOH^{+1} (N_{11}, n_{11}), FeSO_4 (N_{12}, n_{12}), Fe^{+3} (N_{13}, n_{13}), FeOH^{+2} (N_{14}, n_{14}), $\text{Fe}(\text{OH})_2^{+1}$ (N_{15}, n_{15}), $\text{Fe}_2(\text{OH})_2^{+4}$ (N_{16}, n_{16}), FeSO_4^{+1} (N_{17}, n_{17}), $\text{Fe}(\text{SO}_4)_2^{-1}$ (N_{18}, n_{18}), HSO_4^{-1} (N_{19}, n_{19}), SO_4^{-2} (N_{20}, n_{20}), where N_i is the number of entities X_i with mean number n_i of hydrating water particles attached to it, $n_i \geq 0$. Balances for H and O are as follows:

$$\begin{aligned}
 & 2 \cdot N_1 + N_2 \cdot (1 + 2n_2) + N_3 \cdot (1 + 2n_3) + N_4 \cdot (1 + 2n_4) + N_5 \cdot (2 + 2n_5) + N_6 \cdot (1 + 2n_6) + \\
 & N_7 \cdot (1 + 2n_7) + N_8 \cdot 2n_8 + N_9 \cdot 2n_9 + N_{10} \cdot 2n_{10} + N_{11} \cdot (1 + 2n_{11}) + N_{12} \cdot 2n_{12} + \\
 & N_{13} \cdot 2n_{13} + N_{14} \cdot (1 + 2n_{14}) + N_{15} \cdot (2 + 2n_{15}) + N_{16} \cdot (2 + 2n_{16}) + N_{17} \cdot 2n_{17} + N_{18} \cdot 2n_{18} + \\
 & N_{19} \cdot (1 + 2n_{19}) + N_{20} \cdot 2n_{20} = 14 \cdot N_{01} + 2 \cdot N_{02} + 2 \cdot N_{0W} + 2 \cdot N_W
 \end{aligned} \tag{1}$$

$$\begin{aligned}
 &N_1+N_2 \cdot n_2+N_3 \cdot (1+n_3)+N_4 \cdot (1+n_4)+N_5 \cdot (2+n_5)+N_6(2+n_6)+N_7(2+n_7)+ \\
 &N_8 \cdot (2+n_8)+N_9 \cdot (2+n_9)+N_{10} \cdot n_{10}+N_{11}(1+n_{11})+N_{12} \cdot (4+n_{12})+N_{13} \cdot n_{13}+ \\
 &N_{14} \cdot (1+n_{14})+N_{15} \cdot (2+n_{15})+N_{16} \cdot (2+n_{16})+N_{17} \cdot (4+n_{17})+N_{18} \cdot (8+n_{18})+ \\
 &N_{19}(4+n_{19})+N_{20} \cdot (4+n_{20})=11 \cdot N_{01}+2 \cdot N_{02}+N_{0W}+N_W
 \end{aligned} \tag{2}$$

From (1) and (2) we have

$$\begin{aligned}
 &-N_2+N_3+N_4+2N_5+3N_6+3N_7+4N_8+4N_9+N_{11}+8N_{12}+N_{14}+ \\
 &2N_{15}+2N_{16}+8N_{17}+16N_{18}+7N_{19}+8N_{20}=8N_{01}+2N_{02}
 \end{aligned} \tag{3}$$

Adding the sides of (3) and:

$$+N_2-N_3-N_6-N_8+2N_{10}+N_{11}+3N_{13}+2N_{14}+N_{15}+4N_{16}+N_{17}-N_{18}-N_{19}-2N_{20}=0$$

$$6N_{01}=6N_{12}+6N_{17}+12N_{18}+6N_{19}+6N_{20}$$

after cancellation of similar terms, one obtains the relation

$$\begin{aligned}
 &N_4+2N_5+2N_6+3N_7+3N_8+4N_9+2N_{10}+2N_{11}+2N_{12}+ \\
 &3N_{13}+3N_{14}+3N_{15}+6N_{16}+3N_{17}+3N_{18}=2N_{01}+2N_{02}
 \end{aligned} \tag{4}$$

Dividing the sides of (6) by $N_A \cdot V_0$, we get the simple form of GEB related to this system

$$\begin{aligned}
 &[\text{OH}] + 2 \cdot ([\text{H}_2\text{O}_2] + [\text{HO}_2^{-1}]) + 3 \cdot ([\text{HO}_2] + [\text{O}_2^{-1}]) + 4 \cdot [\text{O}_2] + \\
 &2 \cdot ([\text{Fe}^{+2}] + [\text{FeOH}^{+1}] + [\text{FeSO}_4]) + 3 \cdot ([\text{Fe}^{+3}] + [\text{FeOH}^{+2}] + [\text{Fe}(\text{OH})_2^{+1}] + \\
 &2 \cdot [\text{Fe}_2(\text{OH})_2^{+4}] + [\text{FeSO}_4^{+1}] + [\text{Fe}(\text{SO}_4)_2^{-1}]) = 2 \cdot C_{01} + 2 \cdot C_{02}
 \end{aligned} \tag{5}$$

where $[X_i] = N_i / (N_A \cdot V_0)$, $C_{0j} = N_{0j} / (N_A \cdot V_0)$. Hydrating water particles at the corresponding species X_i are omitted in (5), for simplicity of notation. Eq. (5) involves only the elements participating redox equilibria; the electrons of sulfur in sulfate species do not participate the redox equilibria. Note that the radical species (OH, HO₂) are involved in (5), and O₂ is the biradical.

For redox systems, the balance obtained according to the second approach can be transformed into the form ascribed to the first approach. However, in the second approach we are not forced to define/calculate oxidation degrees of elements; it is a very advantageous occurrence, of capital importance for the systems with complex organic compounds, their ions and/or radicals.

5.1.2 A generalizing notation

Let us consider the electrolytic system, where the species of $\text{H}_p\text{O}_q\text{X}_r^{+z} \cdot n_{\text{pq}rz}\text{H}_2\text{O}$ type ($z = z_{\text{pq}rz} = 0, \pm 1, \pm 2, \dots; n_{\text{pq}rz} \geq 0$) are formed after introducing the substance $\text{H}_p\text{O}_q\text{X}_r \cdot n\text{H}_2\text{O}$ into water. From comparison of the elemental balances, we get the equation (Michałowski, 2010)

$$\sum_{\text{pq}rz} (r \cdot Z_X + p - 2q - z) \cdot [\text{H}_p\text{O}_q\text{X}_r^{+z} \cdot n_{\text{pq}rz}\text{H}_2\text{O}] = (R \cdot Z_X + P - 2Q) \cdot C \tag{6}$$

where Z_X is the atomic number for the element X; the set of indices (p,q,r,z) covered by the sum in (6) is different from: (2,1,0,0) for H₂O, (1,0,0,1) for H⁺¹, and (1,1,0,-1) for OH⁻¹. It is assumed that $\text{H}_p\text{O}_q\text{X}_r \cdot n\text{H}_2\text{O}$ does not react (as oxidizing or reducing agent) with water, i.e. products of water oxidation or reduction are not formed. For example, after introducing Br₂ (X = Br; P=Q=n=0, R=2; $Z_X = Z_{\text{Br}} = 35$) into water, the following bromine species are formed

as hydrates in the disproportionation process: HBrO_3 ($p=r=1, q=3, z=0$), BrO_3^{-1} ($p=0, r=1, q=3, z=-1$), HBrO ($p=q=r=1, z=0$), BrO^{-1} ($p=0, q=r=1, z=-1$), Br_2 ($p=q=z=0, r=2$), Br_3^{-1} ($p=q=0, r=3, z=-1$), Br^{-1} ($p=q=0, r=1, z=-1$). Applying Eq. 6, we get (Michałowski, 1994)

$$\begin{aligned} (Z_{\text{Br}}-5)([\text{HBrO}_3]+[\text{BrO}_3^{-1}])+(Z_{\text{Br}}-1)([\text{HBrO}]+[\text{BrO}^{-1}])+2Z_{\text{Br}}[\text{Br}_2]+ \\ (3Z_{\text{Br}}+1)[\text{Br}_3^{-1}]+(Z_{\text{Br}}+1)[\text{Br}^{-1}]=2Z_{\text{Br}}\cdot C \end{aligned} \quad (7)$$

where C [mol/L] is the total concentration of Br_2 . In (7), hydrating water particles are omitted, for simplicity.

For comparative purposes, one can refer to (a) Br_2 (C) + KBr (C_1); (b) NaBrO (C_2); (c) KBrO_3 (C_3) + KBr (C_1) solutions. In all instances, the left side of (7) is identical, whereas the right side is as follows: $2Z_{\text{Br}}C + (Z_{\text{Br}}+1)C_1$ for (a); $(Z_{\text{Br}}-1)C_2$ for (b); $(Z_{\text{Br}}-5)C_3 + (Z_{\text{Br}}+1)C_1$ for the case (c).

5.2 Dynamic redox systems

In physicochemical/analytical practice, a dynamic system is usually realized according to titrimetric mode, where V mL of titrant (T) is added into V_0 mL of titrand (D). Assuming additivity in volumes, V_0+V of D+T system is thus formed. In common redox titrations, two or more elements, represented by different species, can participate redox equilibria.

5.2.1 $\text{FeSO}_4+\text{H}_2\text{SO}_4+\text{KMnO}_4$

This system be referred to titration of V_0 mL D, composed of FeSO_4 (C_0) + H_2SO_4 (C_1), with V mL of C mol/L KMnO_4 as T. The electron balance (GEB) has the form ($Z_1 = 25$ for Mn, $Z_2 = 26$ for Fe):

$$\begin{aligned} (Z_1-7)[\text{MnO}_4^{-1}] + (Z_1-6)[\text{MnO}_4^{-2}] + (Z_1-3)([\text{Mn}^{+3}] + [\text{MnOH}^{+2}] + \\ \gamma_1[\text{MnSO}_4^{+1}] + \gamma_2[\text{Mn}(\text{SO}_4)_2^{-1}]) + (Z_1-2)([\text{Mn}^{+2}] + [\text{MnOH}^{+1}] + [\text{MnSO}_4]) + \\ (Z_2-2)([\text{Fe}^{+2}] + [\text{FeOH}^{+1}] + [\text{FeSO}_4] + (Z_2-3)([\text{Fe}^{+3}] + [\text{FeOH}^{+2}] + [\text{Fe}(\text{OH})_2^{+1}] + \\ 2[\text{Fe}_2(\text{OH})_2^{+4}] + [\text{FeSO}_4^{+1}] + [\text{Fe}(\text{SO}_4)_2^{-1}]) - ((Z_2-2)C_0V_0 + (Z_1-7)CV)/(V_0+V) = 0 \end{aligned} \quad (8)$$

The symbols: γ_1 and γ_2 in (8) are referred to the pre-assumed sulphate complexes (see Fig. 18A); $\gamma_1 = 1, \gamma_2 = 0$ if only MnSO_4^{+1} is pre-assumed, and $\gamma_1 = \gamma_2 = 1$ if both (MnSO_4^{+1} and $\text{Mn}(\text{SO}_4)_2^{-1}$) complexes be pre-assumed.

5.2.2 $\text{KIO}_3+\text{HCl}+\text{H}_2\text{SeO}_3(+\text{HgCl}_2)+$ ascorbic acid

An interesting/spectacular example is the titration of V_0 mL of D containing KIO_3 (C_0 mol/L) + HCl (C_a mol/L) + H_2SeO_3 (C_{Se} mol/L) + HgCl_2 (C_{Hg} mol/L) with V mL of C mol/L ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) as T. For example, the electron balance (GEB) referred to this system can be written as follows (Michałowski, 2010):

$$\begin{aligned} (Z_1+1)[\text{I}^{-1}]+(3Z_1+1)[\text{I}_3^{-1}]+2Z_1([\text{I}_2]+\alpha\cdot[\text{I}_2])+(Z_1-1)([\text{HIO}]+[\text{IO}^{-1}])+(Z_1-5)([\text{HIO}_3]+[\text{IO}_3^{-1}])+ \\ (Z_1-7)([\text{H}_5\text{IO}_6]+[\text{H}_4\text{IO}_6^{-1}]+[\text{H}_3\text{IO}_6^{-2}])+(Z_2-2)([\text{Hg}^{+2}]+[\text{HgOH}^{+1}]+[\text{Hg}(\text{OH})_2]) + \\ (Z_2-2+Z_1+1)[\text{HgI}^{+1}]+(Z_2-2+2(Z_1+1))[\text{HgI}_2]+(Z_2-2+3(Z_1+1))[\text{HgI}_3^{-1}] + \\ (Z_2-2+4(Z_1+1))[\text{HgI}_4^{-2}]+2\gamma\cdot(Z_2-1)([\text{Hg}_2^{+2}]+[\text{Hg}_2\text{OH}^{+1}])+Z_3([\text{C}_6\text{H}_8\text{O}_6]+[\text{C}_6\text{H}_7\text{O}_6^{-1}] + \\ [\text{C}_6\text{H}_6\text{O}_6^{-2}])+(Z_3-2)[\text{C}_6\text{H}_6\text{O}_6]+(Z_4+1)[\text{Cl}^{-1}]+2Z_4[\text{Cl}_2]+(Z_4-1)([\text{HClO}]+[\text{ClO}^{-1}]) + \\ (Z_4-3)([\text{HClO}_2]+[\text{ClO}_2^{-1}])+(Z_4-4)[\text{ClO}_2]+(Z_4-5)[\text{ClO}_3^{-1}]+(Z_4-7)[\text{ClO}_4^{-1}] + \\ (Z_1+Z_4)[\text{ICl}]+(Z_1+2(Z_4+1))[\text{ICl}_2^{-1}]+(2Z_1+Z_4+1)[\text{I}_2\text{Cl}^{-1}]+(Z_2-2+Z_4+1)[\text{HgCl}^{+1}] + \\ (Z_2-2+2(Z_4+1))[\text{HgCl}_2]+(Z_2-2+3(Z_4+1))[\text{HgCl}_3^{-1}]+(Z_2-2+4(Z_4+1))[\text{HgCl}_4^{-2}] + \\ (Z_5-4)\{[\text{H}_2\text{SeO}_3]+[\text{HSeO}_3^{-1}]+[\text{SeO}_3^{-2}]\}+\beta\cdot(Z_5-6)([\text{HSeO}_4^{-1}]+[\text{SeO}_4^{-2}]) - \\ ((Z_1-5)C_0V_0+\gamma(Z_2-2+2(Z_4+1))C_{\text{Hg}}V_0+Z_3CV+(Z_4+1)C_aV_0+\beta(Z_5-4)C_{\text{Se}}V_0)/(V_0+V)=0 \end{aligned} \quad (9)$$

where Z_1, Z_2, Z_4, Z_5 are atomic numbers for I, Hg, Cl and Se, respectively; Z_3 is the number ascribed to ascorbic acid. The following terms were introduced in there:

- $\alpha = 1$, valid under assumption that solid iodine (I_2) is present in the system considered; $\alpha = 0$, for a system not saturated against solid iodine (I_2 refers to soluble form of iodine);
- $\beta = 1$ refers to the case, where Se(VI) species were involved; at $\beta = 0$, the Se(VI) species are omitted;
- $\gamma = 1$ refers to the case, where Hg(I) species were involved; at $\gamma = 0$, the Hg(I) species are omitted.

6. Charge and concentration balances

The set of balances referred to non-redox systems consists of charge and concentration balances. For redox systems, this set is supplemented by electron balance (GEB). For example, the charge and concentration balances referred to C mol/L Br_2 (see section 5.1.2)

$$[H^{+1}] - [OH^{-1}] - [BrO_3^{-1}] - [BrO^{-1}] - [Br_3^{-1}] - [Br^{-1}] = 0 \quad (10)$$

$$[HBrO_3] + [BrO_3^{-1}] + [HBrO] + [BrO^{-1}] + 2[Br_2] + 3[Br_3^{-1}] + [Br^{-1}] = 2C \quad (11)$$

are supplemented by Eq. (7), i.e. (7), (10) and (11) form the complete set of balances related to aqueous solution of Br_2 (C mol/L).

Charge and concentration balances referred to the systems 5.2.1 and 5.2.2 are specified in (Michałowski and Lesiak, 1994b, Michałowski et al., 1996) and (Michałowski and Lesiak, 1994b, Michałowski, 2010), respectively. For example, the species involved in the system 5.2.2 enter $s+2 = 7$ balances: GEB, charge balance, and five concentration balances; K^{+1} ions, as a sole potassium species in this system, enters simply the related charge balance, i.e. concentration balance for K^{+1} is not formulated. Generally, concentration balances are not formulated for the species not participating other (acid-base, complexation, precipitation or redox) equilibria in the system considered.

7. Equilibrium constants

Different species in the system are interrelated in expressions for the corresponding equilibrium constants, e.g., ionic product of water, dissociation constants (for acidic species), stability constants of complexes, solubility products, standard potentials (E_{0i}) for redox reactions, partition constants in liquid-liquid extraction systems. Except E_{0i} , all equilibrium constants are formulated immediately on the basis of mass action law.

The redox systems are completed by relations for standard potentials (E_{0i}), formulated on the basis of the Nernst equation for potential E, referred to i-th redox reaction notation, written in the form $\dots + z_i e^{-1} = \dots$, where $z_i > 0$ is the number of electrons (e^{-1}) participating this reaction. First, the equilibrium constant (K_{ei}) for the redox reaction is formulated on the basis of mass action law and then the relations:

$$K_{ei} = 10^{z_i \cdot E_{0i} / S} \quad \text{and} \quad [e^{-1}] = 10^{-E/S} \quad (12)$$

are applied, where $S = RT/F \cdot \ln 10$, and T, R, F are as ones in the Nernst equation. Both types of constraints, i.e. balances and the expressions for equilibrium constants, are of algebraic

nature. It enables to consider the relations as common algebraic equations, nonlinear in their nature.

In order to avoid inconsistency between the equilibrium constants values found in literature, the set of independent equilibrium constants is required. One should also be noted that some species are presented differently, see e.g., pairs: AlO_2^{-1} and $\text{Al}(\text{OH})_4^{-1}$; $\text{H}_2\text{BO}_3^{-1}$ and $\text{B}(\text{OH})_4^{-1}$; IO_4^{-1} and $\text{H}_4\text{IO}_6^{-1}$, differing in the number of water molecules involved. The species compared here should be perceived as identical ones and then cannot enter the related balances, side by side, as independent species.

The balances and complete set of interrelations resulting from expressions for independent equilibrium constants are the basis for calculations made according to an iterative computer program, e.g., MATLAB. The results thus obtained can be presented graphically, at any pre-assumed system of coordinates, in 2D or 3D space.

The procedure involved with the terms β and γ expresses the principle of "variation on the subject" applied to the system in question. The system considered in 5.2.2 is described with use of the set of 36 independent equilibrium constants in the basic version, i.e. at $\beta=\gamma=0$. More equilibrium data are involved, if some "variations on the subject" be done, i.e. when some reaction paths are liberated. In the "variations" of this kind, further physicochemical data are applied (see section 11.2).

8. Calculation procedure

The balances, related to a dynamic system and realised according to titrimetric mode, can be written as a set of algebraic equations

$$F_k(\mathbf{x}(V))=0 \quad (13)$$

where $\mathbf{x}(V) = [x_1(V), \dots, x_n(V)]^T$ is the vector of basic (independent, fundamental) variables $x_i = x_i(V)$ (scalars) related to a particular V -value, i.e. volume of titrant added. The number (n) of variables is equal to the number of the balances. At defined V -value, only one vector, $\mathbf{x} = \mathbf{x}(V)$, exists that turns the set of algebraic expressions $F_k(\mathbf{x}(V))$ to zero, i.e. $F_k(\mathbf{x}(V)) = 0$ ($k=1, \dots, n$) and zeroes the sum of squares

$$SS(V) = \sum_{k=1}^n (F_k(\mathbf{x}(V)))^2 = 0 \quad (14)$$

for any V -value. If $\mathbf{x}_s(V)$ is the vector referred to starting (s) values for basic variables related to a particular V -value, then one can expect that $\mathbf{x}_s(V) \neq \mathbf{x}(V)$ and

$$SS(V) = \sum_{k=1}^n (F_k(\mathbf{x}_s(V)))^2 > 0 \quad (15)$$

The searching of $\mathbf{x}(V)$ vector values related to different V , where $F_k(\mathbf{x}(V)) = 0$ ($k=1, \dots, n$), is made according to iterative computer programs, e.g., MATLAB. The searching procedure satisfies the requirements put on optimal $\mathbf{x}(V)$ values, provided that SS value (Eq. 15) is lower than a pre-assumed, sufficiently low positive δ -value, $\delta > 0$, e.g., $\delta = 10^{-14}$, i.e.

$$SS(V) = \sum_{k=1}^n (F_k(\mathbf{x}(V)))^2 < \delta$$

However, the iterative computer programs are (generally) designed for the curve-fitting procedures where the degree of fitting a curve to experimental points is finite. In this case, the criterion of optimisation is based on differences $SS(V,N+1) - SS(V,N)$ between two successive (Nth and N+1th) approximations of $SS(V)$ -value, i.e.

$$|SS(V,N+1)-SS(V,N)|<\delta \quad (16)$$

at a sufficiently low δ -value. However, one should take into account that the inequality (16) can be fulfilled at local minimum different from the global minimum. It can happen if the starting values $x_s(V)$ are too distant from the true value $x(V)$ where the equality (14) is fulfilled. In this case, one should try (repeat) the calculations for new $x_s(V)$ values guessed.

The choice of δ -value depends on the scale of analytical concentrations considered. To 'equalise' the requirements put on particular balances, it is advised to apply 'normalised' balances, obtained by dividing the related balance by total (analytical) concentration involved in this balance.

In all simulated titrations considered below, the following regularities are complied:

1. The independent variables $x_i = x_i(V)$ are introduced as the (negative) powers of 10 (as the base number);

For any $[X] > 0$ one can write $[X] \equiv 10^{\log[X]} = 10^{-pX}$, where $pX = -\log[X]$. One should be noted that $[X] > 0$ for any real pX value, $pX \in \mathfrak{R}$. It particularly refers to protons ($X = H^+$) and electrons (Eq. 12). Such choice of the basic variables improves the course of iteration procedure.

2. The changes in the system are made according to titrimetric mode, with volume V taken as the steering variable.
3. It is advisable to refer the fundamental variables to the species whose concentrations predominate at the start for calculations.

The minimizing procedure starts at the V -value, $V = V_s$, that appears to be 'comfortable' from the user's viewpoint, where the starting $x_s(V)$ values are guessed. Then the optimisation is realised, with negative step put on the V -variable, up to $V = V(\text{begin})$ close to zero value. The possible changes in the phase composition during the iteration procedure should also be taken into account. It particularly refers to formation/disappearance of a solid phase(s) or a change in equilibrium solid phase; the latter problem is raised in section 12. For this purpose, the expressions identical with the forms of the corresponding solubility products should be 'peered' during the simulated procedure. In the system considered in section 5.2.2, the solid iodine, I_2 , is formed within defined V -range.

The results thus obtained enable to calculate all variables of interest. It refers both to fundamental variables such as E , pH and concentrations, and other concentrations of interest. For example, the $Br_2 + H_2O$ (batch) system is described by three balances: (7), (10), (11). In this case, one can choose three fundamental variables: pH , E and pBr , involved with concentrations and referred to negative powers of the base 10: $[H^+] = 10^{-pH}$, $[e^-] = 10^{-E/S}$ (Eq. 12), $[Br^-] = 10^{-pBr}$. Three independent variables involved in three balances give here a unique solution for $(x_1, x_2, x_3) = (pH, E, pBr)$, at a pre-assumed C value (Eq. 11). On this basis, one can calculate concentrations of all other species, e.g.:

$$[BrO_3^-] = 10^{6A(E-1.45)+6pH-pBr}; [Br_2] = 10^{2A(E-1.087)-2pBr} \quad (17)$$

where the fundamental variables are involved; $A = 1/S$ (Eq. 12).

In a simulated titration, as a representation of dynamic system, the set of parameters involve: volume V_0 of D and concentrations of reagents in D and T. Volume V of T is a steering variable/parameter value, at a given point of the titration.

The results of calculations provide the basis for graphical presentation of the data, in 2D or 3D space, that appears to be very useful, particularly in the case of the titrations. The curves for concentrations of different species X_i as a function of volume V are named as speciation curves, plotted usually in semi-logarithmic scale, as the $\log[X_i]$ vs. V relationships. For comparative purposes, it is better to graph the plots as the function of the fraction titrated

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \quad (18)$$

where C_0 is the concentration [mol/L] of analyte A in D of initial volume V_0 , V is the volume [mL] of T added up to a given point of titration, C [mol/L] - concentration of a reagent B (towards A) in T; e.g., for the D+T system presented in section 5.2.2 we have: $A = \text{IO}_3^-$, $B = \text{C}_6\text{H}_8\text{O}_6$. The course of the plots $E = E(V)$ and/or $\text{pH} = \text{pH}(V)$ (or, alternately, $\text{pH} = \text{pH}(\Phi)$ and/or $E = E(\Phi)$) is the basis to indicate the equivalence point(s) according to GEM (Michałowski et al., 2010), with none relevance to the chemical reaction notation.

The plots $\text{pH} = \text{pH}(V)$ and/or $E = E(V)$ can also be obtained experimentally, in potentiometric (pH or E) titrations. Comparing the experimental plots with the related curves obtained in simulated titrations, (a) one can check the validity of physicochemical data applied in calculations, and (b) to do some "variations on the subject" involved with reaction pathways and/or incomplete/doubtful physicochemical data.

9. Graphical presentation of the data referred to redox systems

9.1 Aqueous solutions of Br_2 (batch system)

The properties of aqueous bromine (Br_2 , C mol/L) solutions, considered as a weak acid, are presented in Figures 3a-d, for different C values (Eq. (11)). As we see, E decreases (Fig. 3a) and pH increases with decrease in C value. The pH vs. E relationship is nearly linear in the indicated C -range (Fig. 3c). The Br_2 exists as the predominating bromine species at higher C values (Fig. 3d); it corresponds with the speciation plots presented in Fig. 4.

9.2 Examples of redox titration curves

9.2.1 Titration in $\text{Br}_2 + \text{NaOH}$ and $\text{HBrO} + \text{NaOH}$ systems

As a result of NaOH addition into the solution of (a) Br_2 , (b) HBrO , acid-base and redox reactions proceed simultaneously; a decrease in E is accompanied by pH growth, and significant changes in E and pH at equivalence/stoichiometric points occur, see Figs. 5a,b. Both titrations are involved with disproportionation reactions, formulated on the basis of speciation curves (Fig. 6). From comparison of ordinates at an excess of NaOH we have $\log[\text{BrO}_3^-] - \log[\text{BrO}^-] \approx 4$; i.e. $[\text{BrO}_3^-]/[\text{BrO}^-] \approx 10^4$, and then the effectiveness of reaction



exceeds the effectiveness of reaction



by about 10^4 . Note that the stoichiometries of both reactions are the same, $3 : 6 = 1 : 2$. Concentration of Br^{-1} ions, formed mainly in reaction (19), exceeds $[\text{BrO}_3^{-1}]$ by 5, at higher pH values.

9.2.2 Titration in $\text{I}_2 + \text{NaOH}$ system

The iodine speciation curves related to titration of $V_0 = 100$ mL of D containing iodine (I_2 , 0.01 mol/L) with V mL of $C = 0.1$ mol/L NaOH are presented in Fig. 7. Owing to limited solubility of iodine in water, at $V = 0$, a part of iodine remains as a solid phase, $s < C_0$. This two-phase system exists up to $V = 11.2$ mL; for $V > 11.2$ mL we have $[\text{I}_{2s}] = 0$. In the course of further titration, concentration $[\text{I}_2]$ of dissolved iodine decreases as the result of advancing disproportionation. After crossing the stoichiometric point, i.e. at an excess of NaOH added, the main disproportionation products are: IO_3^{-1} and I^{-1} , formed in the reaction



From Fig. 6 it results that, at an excess of NaOH added, the effectiveness of reaction (20) exceeds the one for reaction



by about $2.5 \cdot 10^9$. The $E = E(V)$ and $\text{pH} = \text{pH}(V)$ curves related to titration of iodine (I_2) in presence/absence of KI in D with NaOH admixed (or not admixed) with CO_2 as T are presented in Figures (5) and (6). The titration curves related to liquid-liquid extraction systems ($\text{H}_2\text{O} + \text{CCl}_4$) were considered in (Michałowski, 1994a).

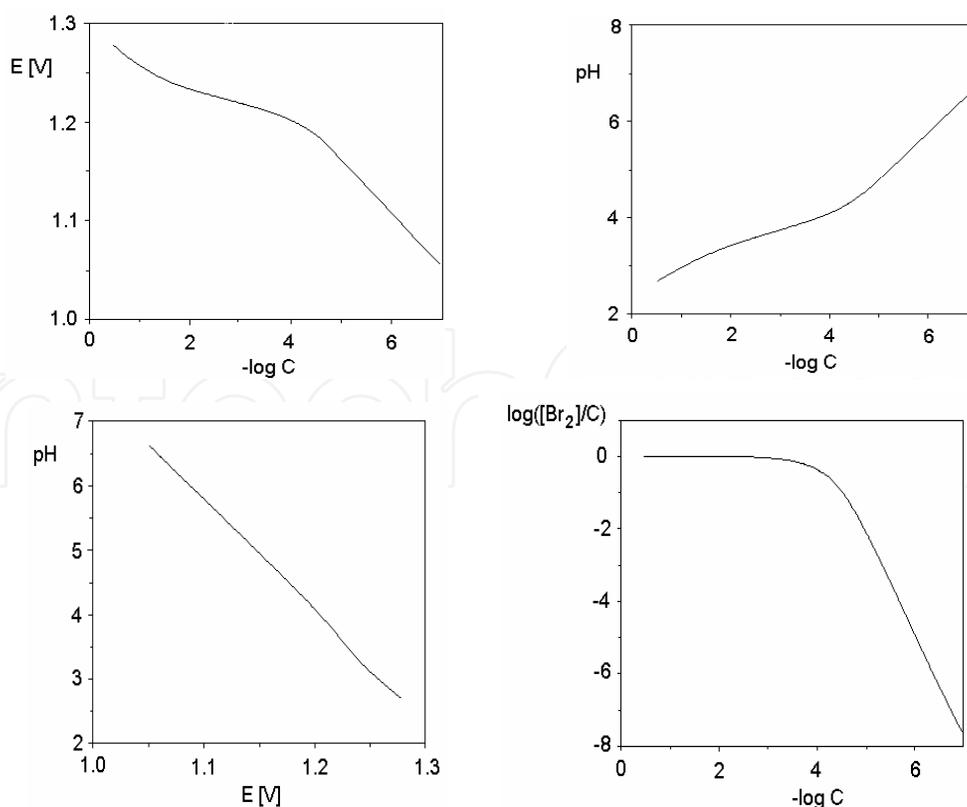


Fig. 3. The curves involved with C mol/L Br_2 solutions in pure water, plotted at the coordinates indicated [4].

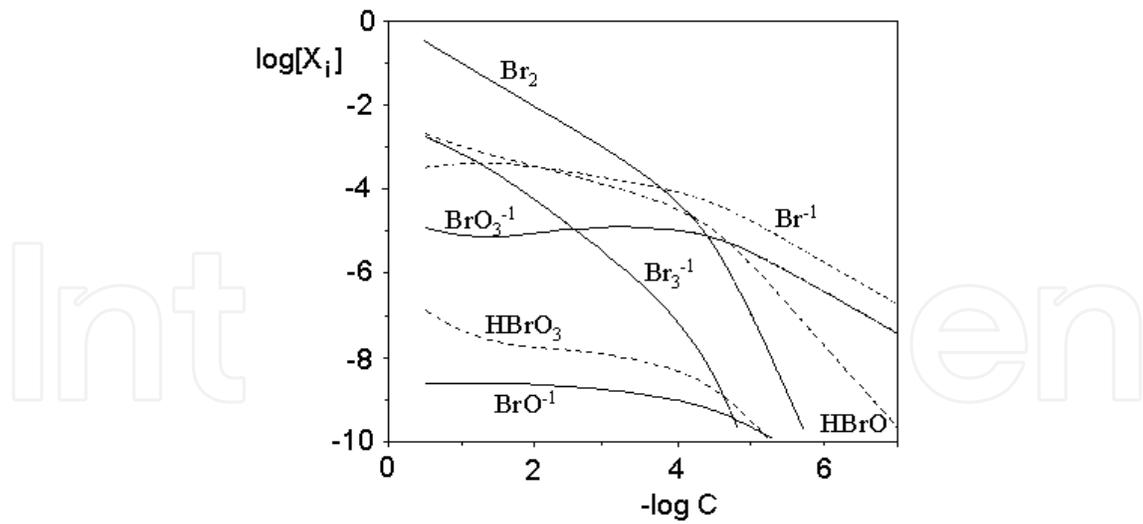


Fig. 4. Concentrations of (indicated) bromine species at different $-\log C$ values for C mol/L Br_2 .

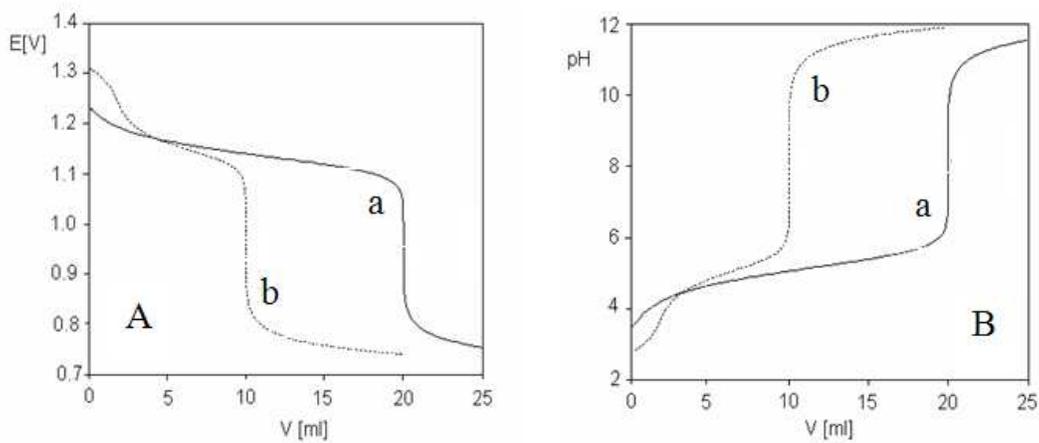


Fig. 5. Theoretical titration curves for: (A) $E = E(V)$ and (B) $\text{pH} = \text{pH}(V)$, at $V_0 = 100$ mL of $C_0 = 0.01$ mol/L (a) Br_2 , (b) HBrO titrated with V mL of $C = 0.1$ mol/L NaOH .

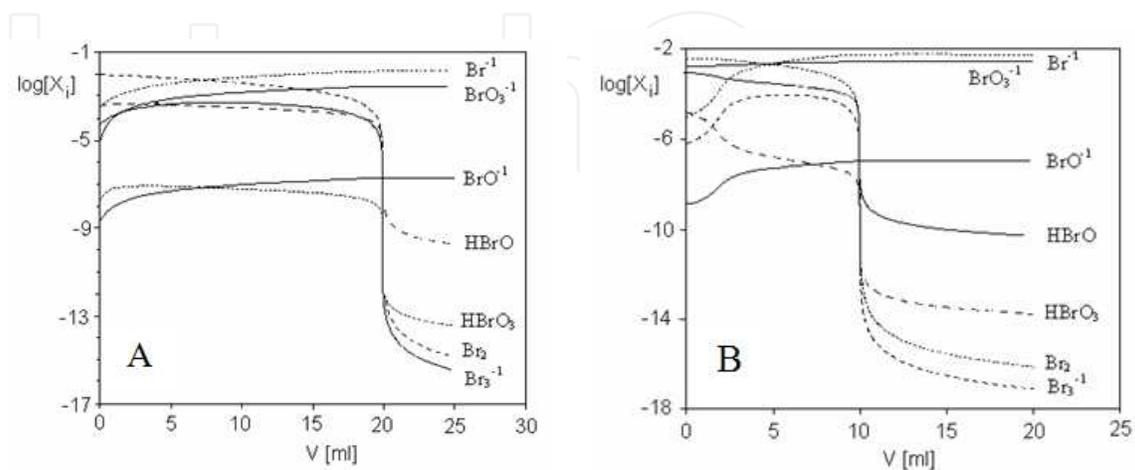


Fig. 6. Speciation of bromine species during titration of $V_0 = 100$ mL of $C_0 = 0.01$ mol/L (A) Br_2 , (B) HBrO titrated with V mL of $C = 0.1$ mol/L NaOH .

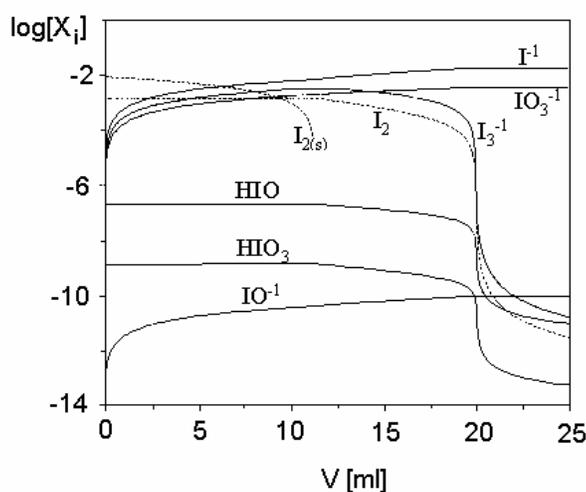


Fig. 7. The speciation curves plotted for $I_2 + NaOH$ system.

9.2.3 Titration of $KIO_3 + KI + H_2SO_4$ with $Na_2S_2O_3$

The pH changes can result from addition of a reagent that - apparently - does not appear, at first sight, acid-base properties. Rather unexpectedly, at first sight, $Na_2S_2O_3$ solution acts on the acidified (H_2SO_4) solution of KIO_3 (or $KIO_3 + KI$) as a strong base (like $NaOH$) see Fig. 8A,B (Michałowski, et al., 1996; Michałowski, et al., 2005). This reaction, known also from qualitative chemical analysis, can be derived from the related speciation plots as

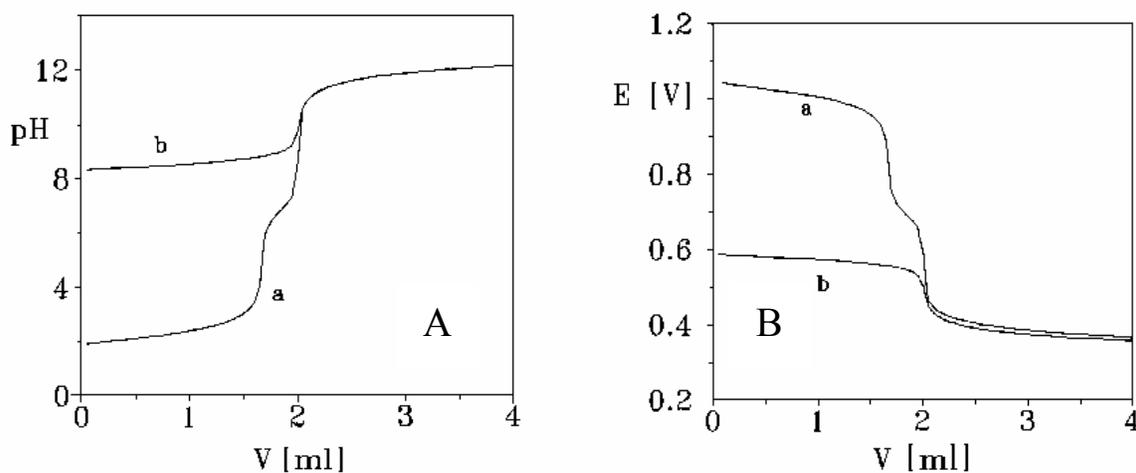
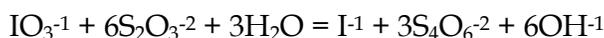


Fig. 8. Theoretical (A) pH vs. V, (B) E vs. V relationships for titration of $V_0 = 100$ mL of KIO_3 (0.05 mol/L) + KI (C_1 mol/L) + H_2SO_4 (0.01 mol/L) as D with $Na_2S_2O_3$ (0.1 mol/L) as T, plotted at $C_1 = 0.1$ mol/L (curve a) and $C_1 = 0$ (curve b).

9.2.4 Titration of $FeSO_4 + H_2SO_4$ with $KMnO_4$

The plots related to the system where $V_0 = 100$ mL of $FeSO_4$ ($C_0 = 0.01$ mol/L) + H_2SO_4 ($C_a = 1.0$ mol/L) is titrated with V mL of $C = 0.02$ mol/L $KMnO_4$ are presented in Fig. 9. It was assumed there that the complexes $MnSO_4^{+1}$ and $Mn(SO_4)_2^{-1}$ are not formed in the system; i.e. $\gamma_1 = \gamma_2 = 0$ in Eq. (8) and in the related concentration balances for Fe, Mn and S.

Fig. 9A indicates the effect resulting from complexation of Fe^{+3} and Fe^{+2} by SO_4^{2-} ions; the course of titration curve a differs significantly from the curve b, where complexes FeSO_4 , FeSO_4^{+1} , $\text{Fe}(\text{SO}_4)_2^{-1}$ and MnSO_4 were omitted in the related balances. The pH change in this system (Fig. 9B) results mainly from consumption of protons in reaction $\text{MnO}_4^{-1} + 8\text{H}^{+1} + 5\text{e}^{-1} = \text{Mn}^{+2} + 4\text{H}_2\text{O}$. Namely, MnO_4^{-1} acts also in acid-base reaction, in multiplied extent when compared with a strong base action, like "octopus" (Michałowski, et al., 2005). Greater pH changes in this system are protected by presence of great excess of H_2SO_4 that acts as buffering agent and acts against formation of solid MnO_2 in reaction $\text{MnO}_4^{-1} + 4\text{H}^{+1} + 3\text{e}^{-1} = \text{MnO}_2 + 2\text{H}_2\text{O}$. The species X_i are indicated at the corresponding dynamic speciation curves plotted in Figures 9C,D.

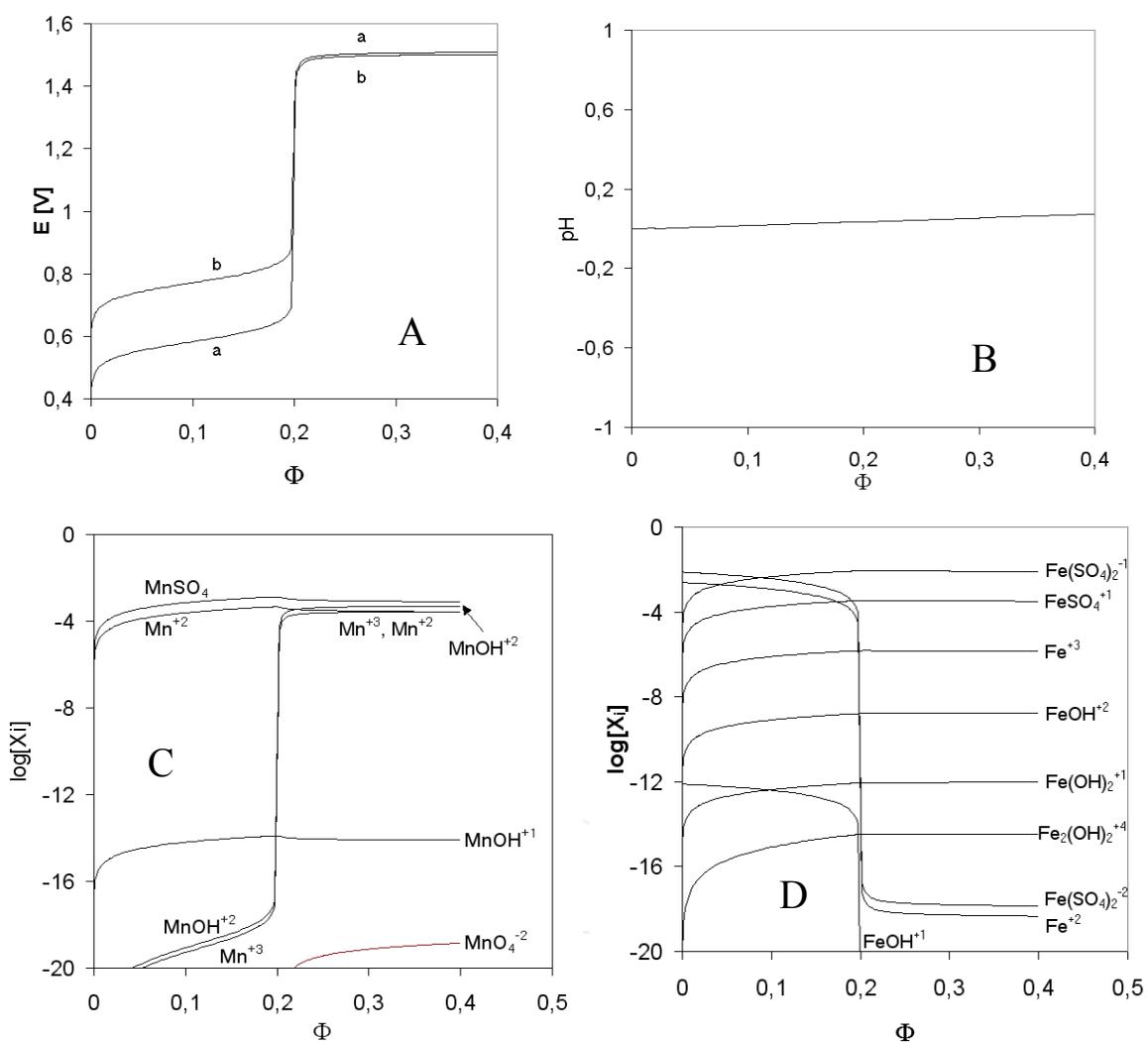


Fig. 9. The plots of (A) $E = E(\Phi)$, (B) $\text{pH} = \text{pH}(\Phi)$ and $\log[X_i]$ vs. Φ relationships for different (C) Mn and (D) Fe species X_i , related to simulated titration presented in section 9.2.4. (Michałowski and Lesiak, 1994b; Michałowski, 2001, 2010)

9.2.5 Titration of $\text{KIO}_3 + \text{HCl} + \text{H}_2\text{SeO}_3 (+\text{HgCl}_2)$ with ascorbic acid

In common redox titrations, two or more elements, represented by different species, can participate redox equilibria. An interesting/spectacular example is the titration of V_0 mL of

D containing KIO_3 ($C_0 = 0.01\text{mol/L}$) + HCl ($C_a = 0.02\text{ mol/L}$) + H_2SeO_3 ($C_{\text{Se}} = 0.02\text{ mol/L}$) + HgCl_2 (C_{Hg} mol/L) with V mL of C mol/L ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) as T, considered e.g., in (Michałowski and Lesiak, 1994b; Michałowski, 2001, 2010). From Fig. 10A,B we see that the presence of HgCl_2 in D transforms the curve a into curve b.

Moreover, Fig. 10b provides (rarely met) example, where pH of the D+T system passes through maximum; such a case was stated first time in (Michałowski and Lesiak, 1994b). The extreme pH values of the curves a and b in Fig. 10B correspond to the points of maximal drop on the curves a and b in Fig.10A. The non-monotonic shapes of pH vs. Φ relationships were also stated e.g., for D+T systems with VSO_4 in acidic (H_2SO_4) media titrated with KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ (Michałowski and Lesiak, 1994b), KI titrated with chlorine water (Michalowski, et al., 1996).

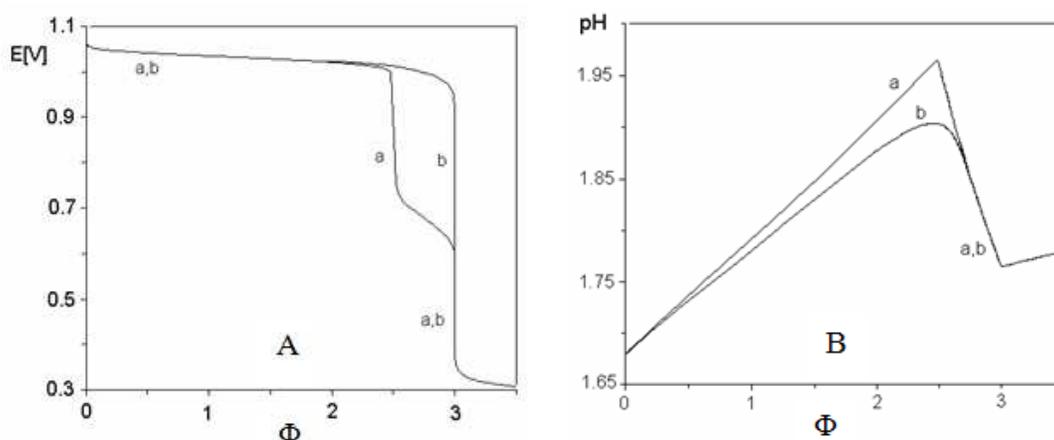


Fig. 10. The plots of: (A) $E = E(\Phi)$ and (B) $\text{pH} = \text{pH}(\Phi)$ relationships for D+T system specified in section 9.2.5, referred to absence (curve a) and presence ($C_{\text{Hg}} = 0.07\text{ mol/L}$, curve b) of HgCl_2 in D.

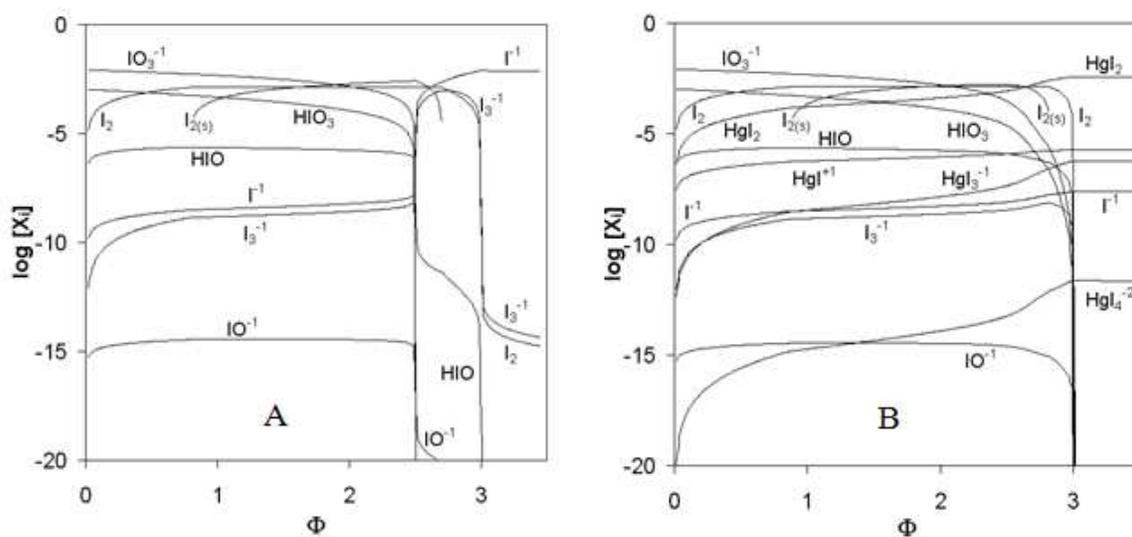
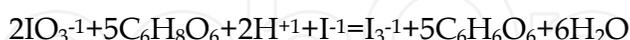
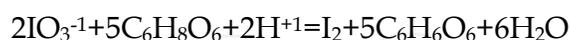
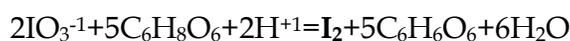


Fig. 11. The plots of speciation curves for different iodine species at $C_0 = 0.01$, $C_a = 0.02$, $C_{\text{Se}} = 0.02$, and $C_{\text{Hg}} = 0$ (in Fig. A) or $C_{\text{Hg}} = 0.07$ (in Fig. B); $\text{I}_{2(\text{s})}$ and I_2 – solid and soluble iodine species.

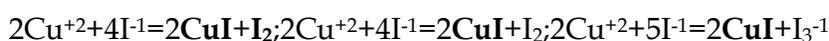
The speciation curves for iodine species in this system are presented in Fig. 11A,B. Among others, on this basis one can state that the growth in pH on the curve a in Fig. 11B within $\Phi \in <0, 2.5>$ can be explained by the set of reactions:



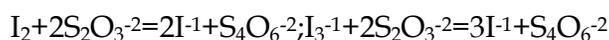
where protons are consumed. This inference results from the fact that within this Φ -interval a growth in concentration of I_2 , I_2 i I_3^{-1} , and decrease in concentration of IO_3^{-1} occur; in this respect, the main components are considered.

10. GATES as a tool for description of multi-step procedure and validation of physicochemical data

This section provides the detailed description of the complex procedure referred to iodometric determination of cupric ions. According to the procedure applied in this method, acidic (H_2SO_4) solution of CuSO_4 is neutralized first with NH_3 solution until the blue colour of the solution, resulting from presence of $\text{Cu}(\text{NH}_3)_i^{+2}$ species, is attained. Then acetic acid is added in excess, to secure pH ca. 3.5. The resulting solution is treated with an excess of KI, forming the precipitate of **CuI**:



At a due excess of KI, I_2 is not formed. The mixture (D) thus obtained is titrated with sodium thiosulphate solution as T:



Let us assume that $V_0 = 100$ ml of the solution containing CuSO_4 ($C_0 = 0.01$ mol/L), H_2SO_4 ($C_a = 0.1$ mol/L), NH_3 ($C_N = 0.25$ mol/L) and CH_3COOH ($C_{Ac} = 0.75$ mol/L), be treated with $V_1 = 5.8$ mL of $C_1 = 2.0$ mol/L KI and then titrated with V ml of $C = 0.1$ mol/L $\text{Na}_2\text{S}_2\text{O}_3$.

On the first stage (Fig.12), we apply the following balances, $F_i = F_i(\mathbf{x}(V)) = 0$ (c^0 - current concentration of **CuI**):

$$F_1 = c^0 + [\text{Cu}^{+1}] + [\text{CuNH}_3^{+1}] + [\text{Cu}(\text{NH}_3)_2^{+1}] + [\text{CuI}_2^{-1}] + [\text{Cu}^{+2}] + [\text{CuOH}^{+1}] + [\text{Cu}(\text{OH})_2] + [\text{Cu}(\text{OH})_3^{-1}] + [\text{Cu}(\text{OH})_4^{-2}] + [\text{CuSO}_4] + [\text{CuIO}_3^{+1}] + [\text{CuNH}_3^{+2}] + [\text{Cu}(\text{NH}_3)_2^{+2}] + [\text{Cu}(\text{NH}_3)_3^{+2}] + [\text{Cu}(\text{NH}_3)_4^{+2}] + [\text{CuCH}_3\text{COO}^{+1}] + [\text{Cu}(\text{CH}_3\text{COO})_2] - C_0V_0 / (V_0 + V) = 0 \quad (21)$$

$$F_2 = c^0 + [\text{I}^{-1}] + 2([\text{I}_2] + \alpha \cdot [\text{I}_2]) + 3[\text{I}_3^{-1}] + [\text{HIO}] + [\text{IO}^{-1}] + [\text{HIO}_3] + [\text{IO}_3^{-1}] + [\text{H}_5\text{IO}_6] + [\text{H}_4\text{IO}_6^{-1}] + [\text{H}_3\text{IO}_6^{-2}] + 2[\text{CuI}_2^{-1}] + [\text{CuIO}_3^{+1}] - C_1V / (V_0 + V) = 0 \quad (22)$$

$$F_3 = [\text{HSO}_4^{-1}] + [\text{SO}_4^{-2}] + [\text{CuSO}_4] - (C_0 + C_a)V_0 / (V_0 + V) = 0 \quad (23)$$

$$F_4 = [\text{NH}_4^{+1}] + [\text{NH}_3] + [\text{CuNH}_3^{+1}] + 2[\text{Cu}(\text{NH}_3)_2^{+1}] + [\text{CuNH}_3^{+2}] + 2[\text{Cu}(\text{NH}_3)_2^{+2}] + 3[\text{Cu}(\text{NH}_3)_3^{+2}] + 4[\text{Cu}(\text{NH}_3)_4^{+2}] - C_NV_0 / (V_0 + V) = 0 \quad (24)$$

$$F_5 = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^{-1}] + [\text{CuCH}_3\text{COO}^{+1}] + 2[\text{Cu}(\text{CH}_3\text{COO})_2] - C_{\text{Ac}}V_0 / (V_0 + V) = 0 \quad (25)$$

$$F_6 = [\text{H}^{+1}] - [\text{OH}^{-1}] + [\text{Cu}^{+1}] - [\text{CuI}_2^{-1}] + 2[\text{Cu}^{+2}] + [\text{CuOH}^{+1}] - [\text{Cu}(\text{OH})_3^{-1}] - 2[\text{Cu}(\text{OH})_4^{-2}] + [\text{CuIO}_3^{+1}] - [\text{I}^{-1}] - [\text{I}_3^{-1}] - [\text{IO}^{-1}] - [\text{IO}_3^{-1}] - [\text{H}_4\text{IO}_6^{-1}] - 2[\text{H}_3\text{IO}_6^{-2}] - [\text{HSO}_4^{-1}] - 2[\text{SO}_4^{-2}] + [\text{CuNH}_3^{+1}] + [\text{Cu}(\text{NH}_3)_2^{+1}] + 2[\text{CuNH}_3^{+2}] + 2[\text{Cu}(\text{NH}_3)_2^{+2}] + 2[\text{Cu}(\text{NH}_3)_3^{+2}] + 2[\text{Cu}(\text{NH}_3)_4^{+2}] + [\text{CuCH}_3\text{COO}^{+1}] + C_1V / (V_0 + V) - [\text{CH}_3\text{COO}^{-1}] + [\text{NH}_4^{+1}] = 0 \quad (26)$$

$$F_7 = (Z_1 - 1 + Z_2 + 1)c^0 + (Z_1 - 1)([\text{Cu}^{+1}] + [\text{CuNH}_3^{+1}] + [\text{Cu}(\text{NH}_3)_2^{+1}]) + (Z_1 - 1 + 2(Z_2 + 1))[\text{CuI}_2^{-1}] + (Z_1 - 2)([\text{Cu}^{+2}] + [\text{CuOH}^{+1}] + [\text{Cu}(\text{OH})_2] + [\text{Cu}(\text{OH})_3^{-1}] + [\text{Cu}(\text{OH})_4^{-2}] + [\text{CuSO}_4] + [\text{CuNH}_3^{+2}] + [\text{Cu}(\text{NH}_3)_2^{+2}] + [\text{Cu}(\text{NH}_3)_3^{+2}] + [\text{Cu}(\text{NH}_3)_4^{+2}] + [\text{CuCH}_3\text{COO}^{+1}] + [\text{Cu}(\text{CH}_3\text{COO})_2]) + (Z_1 - 2 + Z_2 - 5)[\text{CuIO}_3^{+1}] + (Z_2 + 1)[\text{I}^{-1}] + (3Z_2 + 1)[\text{I}_3^{-1}] + 2Z_2([\text{I}_2] + \alpha \cdot [\text{I}_2]) + (Z_2 - 1)([\text{HIO}] + [\text{IO}^{-1}]) + (Z_2 - 5)([\text{HIO}_3] + [\text{IO}_3^{-1}]) + (Z_2 - 7)([\text{H}_5\text{IO}_6] + [\text{H}_4\text{IO}_6^{-1}] + [\text{H}_3\text{IO}_6^{-2}]) - ((Z_1 - 2)C_0V_0 + (Z_2 + 1)C_1V) / (V_0 + V) = 0 \quad (27)$$

where $Z_1 = 29$ for Cu, $Z_2 = 53$ for I. At high excess of I^{-1} , solid I_2 is not formed, $\alpha = 0$ in (22) and (27).

Concentrations of different species in (22) - (27) are involved in the relations ($A = 1/S$, Eq. (12)):

$$\begin{aligned} [\text{NH}_4^{+1}] &= 10^{9.35} \cdot [\text{H}^{+1}] [\text{NH}_3], \\ [\text{CH}_3\text{COOH}] &= 10^{4.65} \cdot [\text{H}^{+1}] [\text{CH}_3\text{COO}^{-1}], \\ [\text{CuOH}^{+1}] &= 10^7 \cdot [\text{Cu}^{+2}] [\text{OH}^{-1}], \\ [\text{Cu}(\text{OH})_2] &= 10^{13.68} \cdot [\text{Cu}^{+2}] [\text{OH}^{-1}]^2, \\ [\text{Cu}(\text{OH})_3^{-1}] &= 10^{17} \cdot [\text{Cu}^{+2}] [\text{OH}^{-1}]^3, \\ [\text{Cu}(\text{OH})_4^{-2}] &= 10^{18.5} \cdot [\text{Cu}^{+2}] [\text{OH}^{-1}]^4, \\ [\text{CuSO}_4] &= 10^{2.36} \cdot [\text{Cu}^{+2}] [\text{SO}_4^{-2}], \\ [\text{CuIO}_3^{+1}] &= 10^{0.82} \cdot [\text{Cu}^{+2}] [\text{IO}_3^{-1}], \\ [\text{CuI}_2^{-1}] &= 10^{8.85} \cdot [\text{Cu}^{+1}] [\text{I}^{-1}]^2, \\ [\text{CuNH}_3^{+2}] &= 10^{3.39} \cdot [\text{Cu}^{+2}] [\text{NH}_3], \\ [\text{Cu}(\text{NH}_3)_2^{+2}] &= 10^{7.33} \cdot [\text{Cu}^{+2}] [\text{NH}_3]^2, \\ [\text{Cu}(\text{NH}_3)_3^{+2}] &= 10^{10.06} \cdot [\text{Cu}^{+2}] [\text{NH}_3]^3, \\ [\text{Cu}(\text{NH}_3)_4^{+2}] &= 10^{12.03} \cdot [\text{Cu}^{+2}] [\text{NH}_3]^4, \\ [\text{CuNH}_3^{+1}] &= 10^{5.93} \cdot [\text{Cu}^{+1}] [\text{NH}_3], \\ [\text{Cu}(\text{NH}_3)_2^{+1}] &= 10^{10.86} \cdot [\text{Cu}^{+1}] [\text{NH}_3]^2, \\ [\text{CuCH}_3\text{COO}^{+1}] &= 10^{2.24} \cdot [\text{Cu}^{+2}] [\text{CH}_3\text{COO}^{-1}], \\ [\text{Cu}(\text{CH}_3\text{COO})_2] &= 10^{3.3} \cdot [\text{Cu}^{+2}] [\text{CH}_3\text{COO}^{-1}]^2, \\ [\text{I}_2] &= [\text{I}^{-1}]^2 \cdot 10^{2A(E-0.62)}, \\ [\text{I}_3^{-1}] &= [\text{I}^{-1}]^3 \cdot 10^{2A(E-0.545)}, \\ [\text{IO}^{-1}] &= [\text{I}^{-1}] \cdot 10^{2A(E-0.49)+2\text{pH}-28}, \\ [\text{IO}_3^{-1}] &= [\text{I}^{-1}] \cdot 10^{6A(E-1.08)+6\text{pH}}, \\ [\text{HIO}] &= 10^{10.6} \cdot [\text{H}^{+1}] [\text{IO}^{-1}], \\ [\text{HIO}_3] &= 10^{0.79} \cdot [\text{H}^{+1}] [\text{IO}_3^{-1}], \\ [\text{H}_5\text{IO}_6] &= [\text{I}^{-1}] \cdot 10^{8A(E-1.26)+7\text{pH}}, \\ [\text{H}_4\text{IO}_6^{-1}] &= 10^{\text{pH}-3.3} \cdot [\text{H}_5\text{IO}_6], \\ [\text{H}_3\text{IO}_6^{-2}] &= [\text{I}^{-1}] \cdot 10^{8A(E-0.37)+9\text{pH}-126}, \\ [\text{Cu}^{+2}] &= [\text{Cu}^{+1}] \cdot 10^{A(E-0.153)} \end{aligned} \quad (28)$$

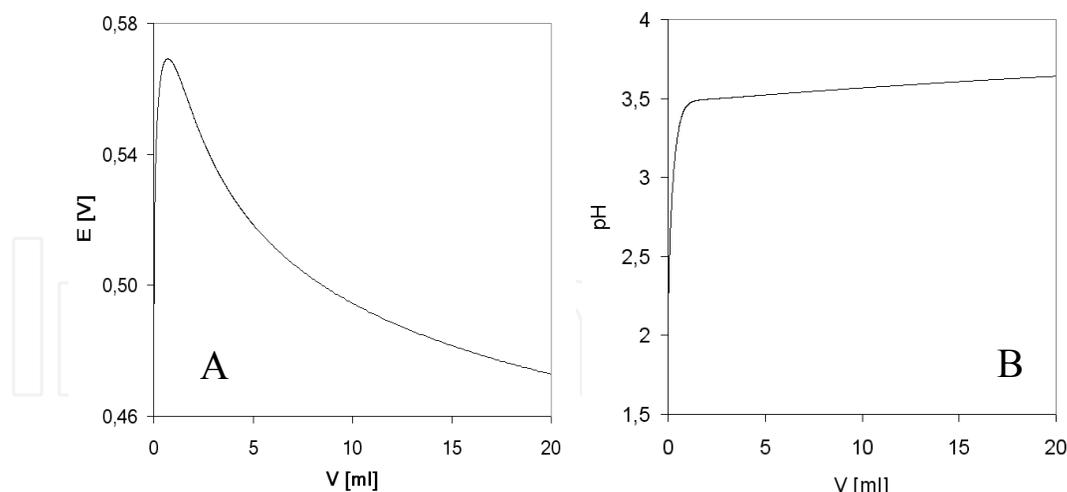


Fig. 12. The (A) E vs. V and (B) pH vs. V relationships during addition of 2.0 mol/L KI into $\text{CuSO}_4 + \text{NH}_3 + \text{HAc}$ system, plotted at $\text{pK}_{\text{so}} = 11.96$.

$$[\text{Cu}^{+1}][\text{I}^{-1}] = K_{\text{so}} \quad (29)$$

On the second stage, we take: $V = V_1$, $V_0' = V_0 + V_1 = 25 + 5.8 = 30.8$ mL, and apply the balances:

$$\begin{aligned} F_1 = & c^0 + [\text{Cu}^{+1}] + [\text{CuNH}_3^{+1}] + [\text{Cu}(\text{NH}_3)_2^{+1}] + [\text{CuI}_2^{-1}] + [\text{Cu}^{+2}] + [\text{CuOH}^{+1}] + \\ & [\text{Cu}(\text{OH})_2] + [\text{Cu}(\text{OH})_3^{-1}] + [\text{Cu}(\text{OH})_4^{-2}] + [\text{CuSO}_4] + [\text{CuIO}_3^{+1}] + [\text{CuNH}_3^{+2}] + \\ & [\text{Cu}(\text{NH}_3)_2^{+2}] + [\text{Cu}(\text{NH}_3)_3^{+2}] + [\text{Cu}(\text{NH}_3)_4^{+2}] + [\text{CuCH}_3\text{COO}^{+1}] + [\text{Cu}(\text{CH}_3\text{COO})_2] + \\ & [\text{CuS}_2\text{O}_3^{-1}] + [\text{Cu}(\text{S}_2\text{O}_3)_2^{-3}] + [\text{Cu}(\text{S}_2\text{O}_3)_3^{-5}] - C_0V_0 / (V_0' + V) = 0 \end{aligned} \quad (30)$$

$$\begin{aligned} F_2 = & c^0 + [\text{I}^{-1}] + 2([\text{I}_2] + \alpha \cdot [\text{I}_2]) + 3[\text{I}_3^{-1}] + [\text{HIO}] + [\text{IO}^{-1}] + \\ & [\text{HIO}_3] + [\text{IO}_3^{-1}] + [\text{H}_5\text{IO}_6] + [\text{H}_4\text{IO}_6^{-1}] + [\text{H}_3\text{IO}_6^{-2}] + \\ & 2[\text{CuI}_2^{-1}] + [\text{CuIO}_3^{+1}] - C_1V_1 / (V_0' + V) = 0 \end{aligned} \quad (31)$$

$$F_3 = [\text{HSO}_4^{-1}] + [\text{SO}_4^{-2}] + [\text{CuSO}_4] - (C_0 + C_a)V_0 / (V_0' + V) = 0 \quad (32)$$

$$\begin{aligned} F_4 = & [\text{NH}_4^{+1}] + [\text{NH}_3] + [\text{CuNH}_3^{+1}] + 2[\text{Cu}(\text{NH}_3)_2^{+1}] + \\ & [\text{CuNH}_3^{+2}] + 2[\text{Cu}(\text{NH}_3)_2^{+2}] + 3[\text{Cu}(\text{NH}_3)_3^{+2}] + \\ & 4[\text{Cu}(\text{NH}_3)_4^{+2}] - C_NV_0 / (V_0' + V) = 0 \end{aligned} \quad (33)$$

$$F_5 = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^{-1}] + [\text{CuCH}_3\text{COO}^{+1}] + 2[\text{Cu}(\text{CH}_3\text{COO})_2] - C_{\text{Ac}}V_0 / (V_0' + V) = 0 \quad (34)$$

$$\begin{aligned} F_6 = & [\text{H}_2\text{S}_2\text{O}_3] + [\text{HS}_2\text{O}_3^{-1}] + [\text{S}_2\text{O}_3^{-2}] + 2[\text{S}_4\text{O}_6^{-2}] + [\text{CuS}_2\text{O}_3^{-1}] + \\ & 2[\text{Cu}(\text{S}_2\text{O}_3)_2^{-3}] + 3[\text{Cu}(\text{S}_2\text{O}_3)_3^{-5}] - CV / (V_0' + V) = 0 \end{aligned} \quad (35)$$

$$\begin{aligned} F_7 = & [\text{H}^{+1}] - [\text{OH}^{-1}] + [\text{Cu}^{+1}] - [\text{CuI}_2^{-1}] + 2[\text{Cu}^{+2}] + [\text{CuOH}^{+1}] - [\text{Cu}(\text{OH})_3^{-1}] - \\ & 2[\text{Cu}(\text{OH})_4^{-2}] + [\text{CuIO}_3^{+1}] - [\text{I}^{-1}] - [\text{I}_3^{-1}] - [\text{IO}^{-1}] - [\text{IO}_3^{-1}] - [\text{H}_4\text{IO}_6^{-1}] - 2[\text{H}_3\text{IO}_6^{-2}] - \\ & [\text{HSO}_4^{-1}] - 2[\text{SO}_4^{-2}] + [\text{CuNH}_3^{+1}] + [\text{Cu}(\text{NH}_3)_2^{+1}] + 2[\text{CuNH}_3^{+2}] + 2[\text{Cu}(\text{NH}_3)_2^{+2}] + \\ & 2[\text{Cu}(\text{NH}_3)_3^{+2}] + 2[\text{Cu}(\text{NH}_3)_4^{+2}] + [\text{CuCH}_3\text{COO}^{+1}] + C_1V_1 / (V_0' + V) - \\ & [\text{CH}_3\text{COO}^{-1}] + [\text{NH}_4^{+1}] + 2CV / (V_0' + V) - [\text{HS}_2\text{O}_3^{-1}] - 2[\text{S}_2\text{O}_3^{-2}] - \\ & 2[\text{S}_4\text{O}_6^{-2}] - [\text{CuS}_2\text{O}_3^{-1}] - 3[\text{Cu}(\text{S}_2\text{O}_3)_2^{-3}] - 5[\text{Cu}(\text{S}_2\text{O}_3)_3^{-5}] = 0 \end{aligned} \quad (36)$$

$$\begin{aligned}
 F_8 = & (Z_1 - 1 + Z_2 + 1)c^0 + (Z_1 - 1)([CuNH_3^{+1}] + [Cu(NH_3)_2^{+1}] + (Z_1 - 1 + 2(Z_2 + 1))[CuI_2^{-1}] + \\
 & (Z_1 - 2)([Cu^{+2}] + [CuOH^{+1}] + [Cu(OH)_2] + [Cu(OH)_3^{-1}] + [Cu(OH)_4^{-2}] \\
 & + [CuSO_4] + [CuNH_3^{+2}] + [Cu(NH_3)_2^{+2}] + [Cu(NH_3)_3^{+2}] + [Cu(NH_3)_4^{+2}] + \\
 & [CuCH_3COO^{+1}] + [Cu(CH_3COO)_2] + (Z_1 - 2 + Z_2 - 5)[CuIO_3^{+1}] + (Z_2 + 1)[I^{-1}] + \\
 & (3Z_2 + 1)[I_3^{-1}] + 2Z_2([I_2] + \alpha \cdot [I_2]) + (Z_2 - 1)([HIO] + [IO^{-1}]) + (Z_2 - 5)([HIO_3] + [IO_3^{-1}]) + \\
 & (Z_2 - 7)([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) + 2(Z_3 - 2)([H_2S_2O_3] + [HS_2O_3^{-1}] + \\
 & [S_2O_3^{-2}]) + 4(Z_3 - 2.5)[S_4O_6^{-2}] + (Z_1 - 1 + 2(Z_3 - 2))[CuS_2O_3^{-1}] + \\
 & (Z_1 - 1 + 4(Z_3 - 2))[Cu(S_2O_3)_2^{-3}] + (Z_1 - 1 + 6(Z_3 - 2))[Cu(S_2O_3)_3^{-5}] - \\
 & ((Z_1 - 2)C_0V_0 + (Z_2 + 1)C_1V_1 + 2(Z_3 - 2)CV) / (V_0' + V) = 0
 \end{aligned}
 \tag{37}$$

where $Z_3 = 16$ for S. The additional relationships are as follows:

$$\begin{aligned}
 [H_2S_2O_3] &= 10^{2.32} \cdot [H^{+1}]^2 [S_2O_3^{-2}], \\
 [HS_2O_3^{-1}] &= 10^{1.72} \cdot [H^{+1}] [S_2O_3^{-2}], \\
 [CuS_2O_3^{-1}] &= 10^{10.3} \cdot [Cu^{+1}] [S_2O_3^{-2}], \\
 [Cu(S_2O_3)_2^{-3}] &= 10^{12.2} \cdot [Cu^{+1}] [S_2O_3^{-2}]^2, \\
 [Cu(S_2O_3)_3^{-5}] &= 10^{13.8} \cdot [Cu^{+1}] [S_2O_3^{-2}]^3, \\
 [S_4O_6^{-2}] &= [S_2O_3^{-2}]^2 \cdot 10^{2A(E-0.09)}
 \end{aligned}
 \tag{38}$$

To perform the calculation, one should choose first the set of independent (fundamental) variables. On the first stage, one can choose the variables: $\mathbf{x} = \mathbf{x}(V) = (x_1, \dots, x_7)$, where $x_i = x_i(V)$, involved in the relations:

$$\begin{aligned}
 x_1 = \text{pH}, \quad x_2 = E, \quad x_3 = -\log[I^{-1}], \quad x_4 = -\log c^0, \\
 x_5 = -\log[SO_4^{-2}], \quad x_6 = -\log[NH_4^{+1}], \quad x_7 = -\log[CH_3COO^{-1}]
 \end{aligned}
 \tag{39}$$

On the second stage, this set should be supplemented by the new variable $x_8 = -\log[S_4O_6^{-2}]$, i.e. $\mathbf{x} = (x_1, \dots, x_8)$.

From calculations it results that addition of KI solution (first stage) causes first a growth followed by a drop in potential value (Fig.12A). It is accompanied by a growth in pH-value (Fig.12B). On the stage of $Na_2S_2O_3$ titration, potential E drops significantly at the vicinity of $\Phi = 1$ (Fig.13A). It is accompanied by a slight growth in pH-value (Fig.13B). Fig.13A

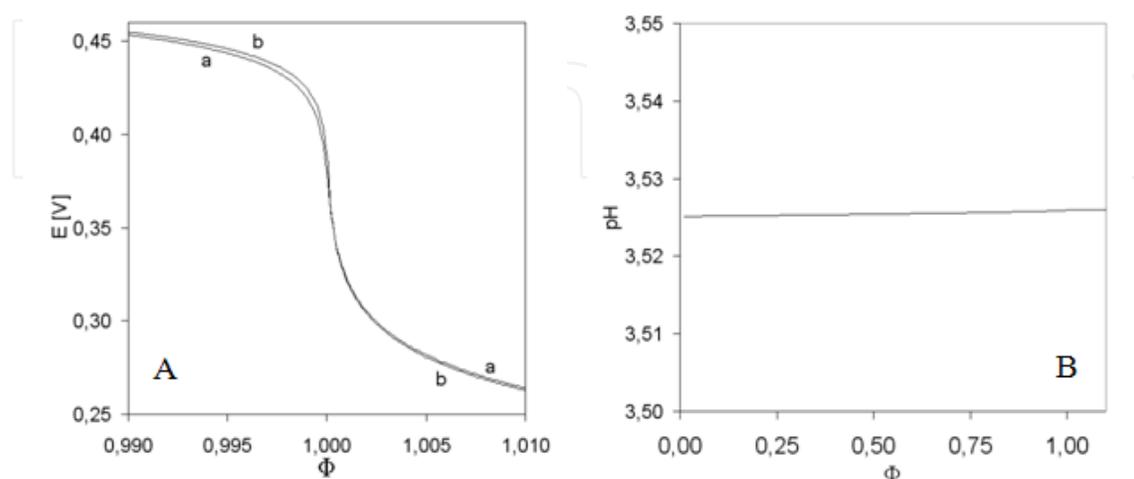


Fig. 13. The (A) E vs. Φ relationships plotted in close vicinity of $\Phi = 1$ at pK_{so} for **CuI** equal (a) 11.96, (b) 12.6 and (b); (B) pH vs. Φ relationship plotted at $pK_{so} = 11.96$.

indicates also a small difference between the plots of the related titration curves, calculated for two pK_{s0} values: 11.96 and 12.6, found in literature. The speciation curves for some species on the stage of titration with $\text{Na}_2\text{S}_2\text{O}_3$ solution, are evidenced in Fig.14. One should be noticed that sulphate and thiosulfate species do not enter the same (elemental) balance, see Eqs. (32) and (35); the thiosulfate species are not oxidised by sulphate, i.e. the synproportionation reaction does not occur.

11. Other possibilities offered by GATES in area of redox systems

Potentiometric titration is a useful/sensitive method that enables, in context with the simulated data obtained according to GATES, to indicate different forbidden paths of chemical reactions. Simply, the shapes of $E = E(\Phi)$ and $\text{pH} = \text{pH}(\Phi)$ functions differ substantially at different assumptions presupposed in this respect. In order to confirm the metastable state according to GATES, one should omit all possible products forbidden by reaction barrier(s) in simulated calculations. Otherwise, one can release some reaction paths and check “what would happen” after inclusion of some species as the products obtained after virtual crossing the related reaction barriers. Such species are included into the balances and involved in the related equilibrium constants. This way one can also explain some phenomena observed during the titration or even ... correct experimental data. Mere errors or inadvertences made in experimental titrations and on the step of graphical presentation of the results, can be indicated this way.

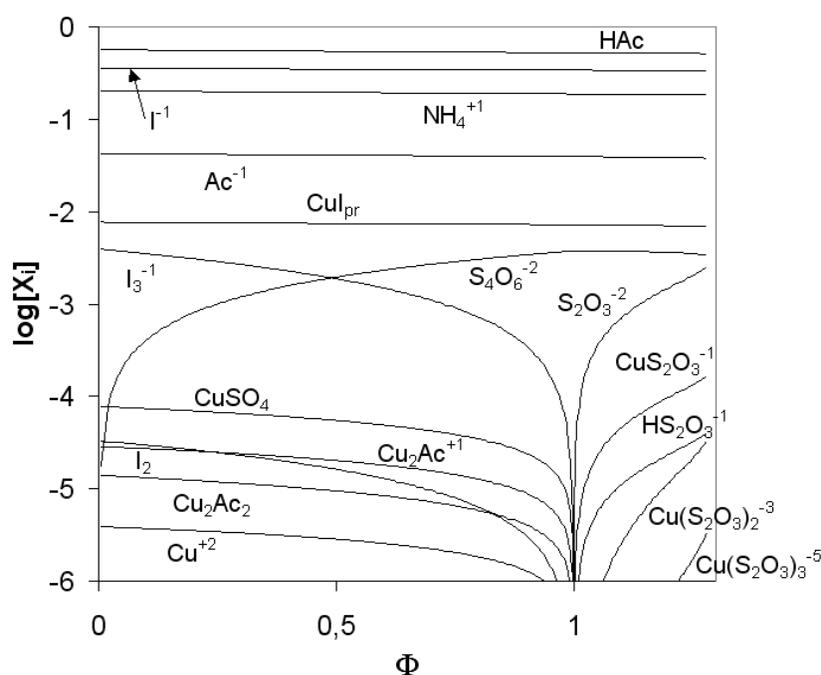


Fig. 14. The speciation curves plotted for titration of $\text{CuSO}_4 + \text{NH}_3 + \text{HAc} + \text{KI}$ with $\text{Na}_2\text{S}_2\text{O}_3$; $pK_{s0} = 11.96$ for CuI ; $\text{HAc} = \text{CH}_3\text{COOH}$.

11.1 GATES as a tool for correction/explanation of experimental data

The effect of HgCl_2 on the shape of titration curves $E = E(\Phi)$, referred to the system 9.2.5, was indicated in Fig. 10A. The shapes of those curves are in accordance with ones obtained

experimentally. Namely, the curve in Fig. 15A is similar to the curve a in Fig. 10A, and the curve in Fig. 15B is similar to the curve b in Fig. 10A.

One can also notice some differences, however. First, the experimental data (potential E values, (1)) obtained in the system with calomel reference electrode were erroneously recalculated (2) when referred to normal hydrogen electrode (NHE scale) (Erdey, et al., 1951/2); simply, the potential of the calomel electrode was subtracted from (not added to) the experimental E-values. These errors were corrected in (Erdey and Svehla, 1973). The theoretical curves in Fig. 10A fall abruptly in the immediate vicinity of $V = 0$. Namely, $E = 1.152$ V at $V = 0$ for the curves a and b; at $V = 0.01$ mL, E equals 1.072 V for A and 1.068 V for B (in NHE scale). In this context one should be noted that the second experimental points in Figs. 15A,B, far distant from $V = 0$, are connected by a rounded line. One can also explain diffused indications in E values, registered in the middle part of the titration curve in Fig. 15A. After comparison with the speciation curves plotted in Figs. 11A,B, one can judge that these fluctuations can be accounted for kinetics of the solid iodine ($I_{2(s)}$) precipitation/dissolution phenomena.

11.2 Testing the reaction paths

Referring again to the system 9.2.5, one can release some reaction paths, particularly the ones involved with oxidation of Se(IV)-species and reduction of Hg(II)-species. The paths are released by setting $\beta = 1$ or/and $\gamma = 1$ in Eq. (9), in charge balance and in concentration balances for Se and Hg. Inspection of the plots presented in Figures 16 and 17, and comparison with the plots in Fig. 10A,B leads to conclusion, that $\beta = \gamma = 0$ in the related balances, i.e. oxidation of Se(IV) and reduction of Hg(II) do not occur during the titration.

11.3 Validation of equilibrium data

Equilibrium data involved with electrolytic systems refer, among others, to stability constants of complexes and solubility products of precipitates. It results from the fact that the equilibrium data values attainable in literature are scattered or unknown.

Some doubts arise when some equilibrium data are unknown on the stage of collection of equilibrium data (Fig. 1). One can also check up the effect involved with omission of some types of complexes.

For example, the curve b plotted in Fig. 9A refers to omission of sulphate complexes in the related balances, referred to the system 9.2.4. The comparison of the corresponding plots provides some doubts related to the oversimplified approach applied frequently in literature. In this system, there were some doubts referred to possible *a priori* complexes of $Mn(SO_4)_i^{+3-2i}$ type; the related stability constants are unknown in literature. To check it, the calculations were made at different stability constants values, K_{3i} , pre-assumed for this purpose, $[Mn(SO_4)_i^{+3-2i}] = K_{3i}[Mn^{+3}][SO_4^{2-}]^i$. From Fig. 18 we see that, at higher K_{3i} values (comparable to ones related to $Fe(SO_4)_i^{+3-2i}$ complexes), the new inflection points appears at $\Phi = 0.25$ and disappears at lower K_{3i} values assumed in the simulating procedure. Comparing the simulated curves with one obtained experimentally, one can conclude that the complexes $Mn(SO_4)_i^{+3-2i}$ do not exist at all or their stability constants are small. Curves a and b in Fig. 13A illustrate the effect of discrepancy between different equilibrium constant values, here: solubility product for **CuI**.

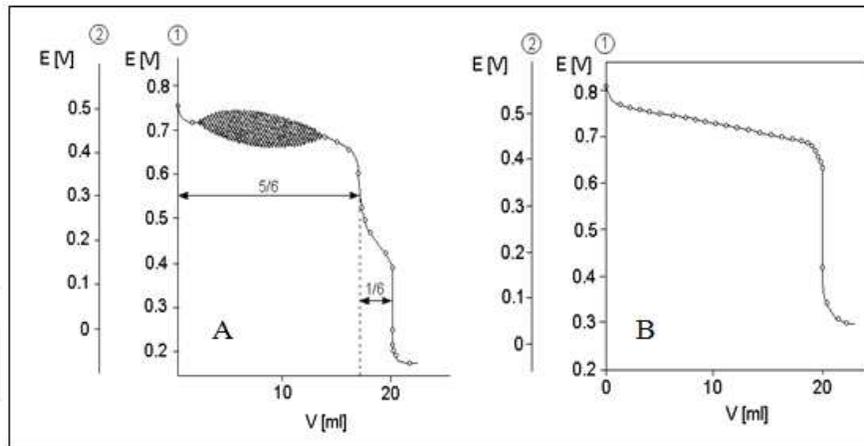


Fig. 15. The experimental titration curves copied from (Erdey, et al., 1951/2).

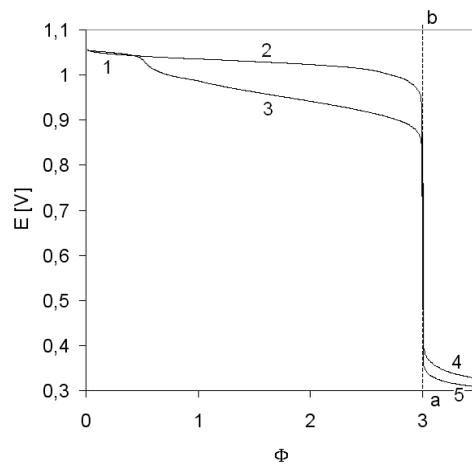


Fig. 16. The E vs. Φ relationships plotted under assumption that (i) $\beta = \gamma = 0$ - curve 125 ; (ii) $\beta = 1, \gamma = 0$ - curve 124; (iii) $\beta = 0, \gamma = 1$ - curve 135; (iv) $\beta = \gamma = 1$ - curve 134; $C_0 = 0.01$, $C_a = 0.02$, $C_{Se} = 0.02$, $C_{Hg} = 0.07$, $C = 0.1$ [mol/L].

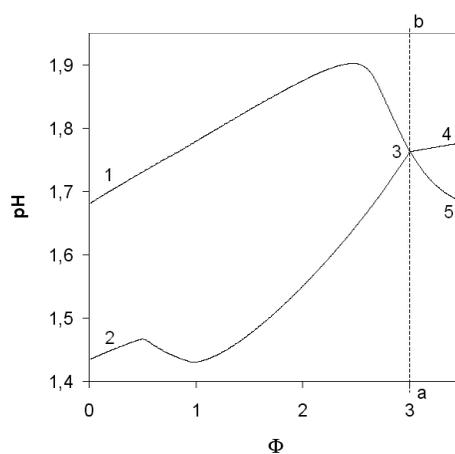


Fig. 17. The pH vs. Φ relationships plotted for the system in section 5.2.2 under assumption that (i) $\beta = \gamma = 0$ - curve 134 ; (ii) $\beta = 1, \gamma = 0$ - curve 135; (iii) $\beta = 0, \gamma = 1$ - curve 234; (iv) $\beta = \gamma = 1$ - curve 235; $C_0 = 0.01$, $C_a = 0.02$, $C_{Se} = 0.02$, $C_{Hg} = 0.07$, $C = 0.1$ [mol/L].

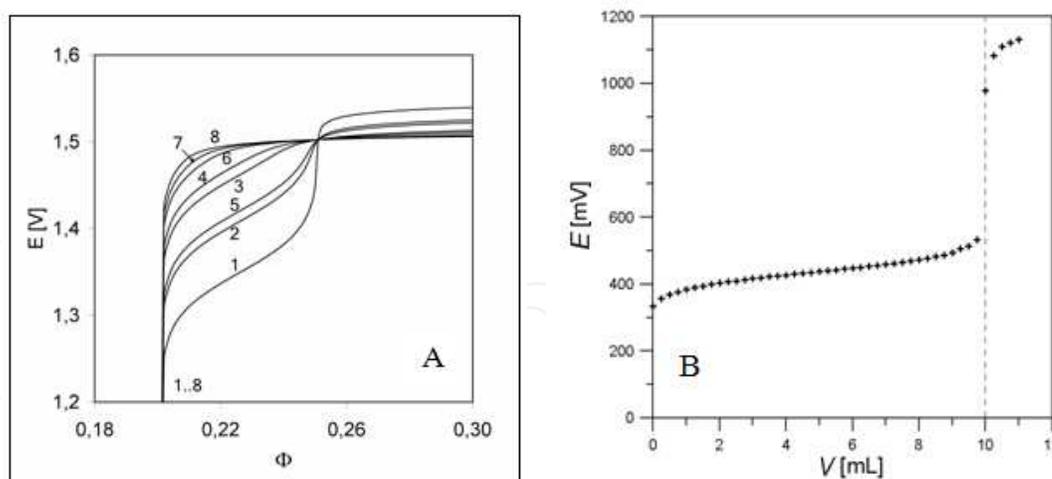


Fig. 18. (A) Fragments of hypothetical titration curves plotted for different pairs of stability constants (K_1 , K_2) of the sulphate complexes $Mn(SO_4)_i^{+3-2i}$: 1 - (10^4 , 10^7), 2 - (10^3 , 10^6), 3 - ($10^{2.5}$, 10^5), 4 - (10^2 , 10^4), 5 - (10^4 , 0), 6 - (10^3 , 0), 7 - (10^2 , 0), 8 - (0, 0) and (B) the titration curve obtained experimentally; $FeSO_4$ ($C_0 = 0.01$ mol/L) + H_2SO_4 ($C_a = 0.1$ mol/L) as D titrated with $C = 0.02$ mol/L $KMnO_4$ as T (Michałowski and Lesiak, 1994b; Michałowski, 2010).

12. Resolution of non-equilibrium two-phase electrolytic batch systems with struvite

Some salts are not the equilibrium solid phases and transform into another solid phases when introduced into pure water or aqueous solution of a strong acid, or a strong base, and/or CO_2 . Such instability characterizes, among others, some ternary salts, such as struvite, $MgNH_4PO_4$ (Michałowski and Pietrzyk, 2006) or dolomite, $MgCa(CO_3)_2$ (Michałowski and al., 2009). Resolution of such systems is realizable within GATES, with use of iterative computer programs, such as MATLAB.

For the study of struvite + aqueous solution system, let us apply the following notations: $pC_0 = -\log C_0$; $pC_{CO_2} = -\log C_{CO_2}$, $pC_b = -\log C_b$; $pr1 = MgNH_4PO_4$, $pr2 = Mg_3(PO_4)_2$, $pr3 = MgHPO_4$, $pr4 = Mg(OH)_2$, $pr5 = MgCO_3$; pri - precipitate of i -th kind ($i = 1, \dots, 5$) with molar concentration $[pri]$; $ppri = -\log [pri]$; K_{soi} - solubility product for pri ($i=1, \dots, 5$).

The instability of struvite in aqueous media can be confirmed in computer simulations, done with use of iterative computer program MATLAB, realized within GATES. The approach to this non-redox system is based on charge and concentration balances, together with expressions for equilibrium constants, involving all physicochemical knowledge on the system in question, collected in (Michałowski and Pietrzyk, 2006). In some instances, the dissolution process consists of several steps, where different solid phases are formed.

12.1 Formulation of the system

The behavior of this system can be followed on the basis of formulation referred to the system where pure $pr1$ is introduced into aqueous solution containing dissolved CO_2 (C_{CO_2} mol/L) + KOH (C_b mol/l) + HCl (C_a); initial ($t = 0$) concentration of $pr1$ in the system equals C_0 mol/L. Taking $ppr1 = -\log [pr1]$ as the steering variable, and denoting $\mathbf{x} = (x_1, \dots, x_5)$ at $C_{CO_2} > 0$, we write the balances $F_i(\mathbf{x}(ppr1)) = 0$ formulated as follows:

$$F_1 = [\text{pr1}] + 3[\text{pr2}] + [\text{pr3}] + [\text{pr4}] + [\text{Mg}^{+2}] + [\text{MgOH}^{+1}] + [\text{MgH}_2\text{PO}_4^{+1}] + [\text{MgHPO}_4] + [\text{MgPO}_4^{-1}] + [\text{MgNH}_3^{+2}] + [\text{Mg}(\text{NH}_3)_2^{+2}] + [\text{Mg}(\text{NH}_3)_3^{+2}] + [\text{MgHCO}_3^{+1}] + [\text{MgCO}_3] - C_0 = 0 \quad (40)$$

$$F_2 = [\text{pr1}] + [\text{NH}_4^{+1}] + [\text{NH}_3] + [\text{MgNH}_3^{+2}] + 2[\text{Mg}(\text{NH}_3)_2^{+2}] + 3[\text{Mg}(\text{NH}_3)_3^{+2}] - C_0 = 0 \quad (41)$$

$$F_3 = [\text{pr1}] + 2[\text{pr2}] + [\text{pr3}] + [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^{-1}] + [\text{HPO}_4^{-2}] + [\text{PO}_4^{-3}] + [\text{MgH}_2\text{PO}_4^{+1}] + [\text{MgHPO}_4] + [\text{MgPO}_4^{-1}] - C_0 = 0 \quad (42)$$

$$F_4 = [\text{H}^{+1}] - [\text{OH}^{-1}] + \Delta + [\text{NH}_4^{+1}] + 2[\text{Mg}^{+2}] + [\text{MgOH}^{+1}] - [\text{HCO}_3^{-1}] - 2[\text{CO}_3^{-2}] + [\text{MgH}_2\text{PO}_4^{+1}] - [\text{MgPO}_4^{-1}] + [\text{MgHCO}_3^{+1}] + 2[\text{MgNH}_3^{+2}] + 2[\text{Mg}(\text{NH}_3)_2^{+2}] + 2[\text{Mg}(\text{NH}_3)_3^{+2}] - [\text{H}_2\text{PO}_4^{-1}] - 2[\text{HPO}_4^{-2}] - 3[\text{PO}_4^{-3}] = 0 \quad (43)$$

$$F_5 = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^{-1}] + [\text{CO}_3^{-2}] + [\text{MgHCO}_3^{+1}] + [\text{MgCO}_3] - C_{\text{CO}_2} = 0 \quad (44)$$

where (in Eq. 43)

$$\Delta = C_b - C_a \quad (45)$$

On defined stage of **pr1** dissolution, concentrations of some (or all) solid phases assumed zero value. To check it, the q_i values:

$$q_1 = [\text{Mg}^{+2}] \cdot [\text{NH}_4^{+1}] \cdot [\text{PO}_4^{-3}] / K_{\text{so1}}; \quad q_2 = [\text{Mg}^{+2}]^3 \cdot [\text{PO}_4^{-3}]^2 / K_{\text{so2}}; \\ q_3 = [\text{Mg}^{+2}] \cdot [\text{HPO}_4^{-2}] / K_{\text{so3}}; \\ q_4 = [\text{Mg}^{+2}] \cdot [\text{OH}^{-1}]^2 / K_{\text{so4}}; \quad q_5 = [\text{Mg}^{+2}] \cdot [\text{CO}_3^{-2}] / K_{\text{so5}} \quad (46)$$

for different potentially precipitable species pri ($i=1, \dots, 5$) were 'peered' in computer program applied for this purpose.

Concentration of MgCO_3 , i.e. **pr5**, has not been included in the concentration balances (40) and (44) specified above. Simply, from the preliminary calculations it was stated that, at any case considered below, **pr5** does not exist as the equilibrium solid phase.

At the start for calculations, the fundamental variables were chosen, namely:

$$x_1 = \text{pMg} = -\log[\text{Mg}^{+2}], \quad x_2 = \text{pNH}_3 = -\log[\text{NH}_3], \\ x_3 = \text{pHPO}_4 = -\log[\text{HPO}_4^{-2}], \\ x_4 = \text{pH}, \quad x_5 = \text{pHCO}_3 = -\log[\text{HCO}_3^{-1}] \quad (47)$$

At $C_{\text{CO}_2} = 0$ ($\text{pC}_{\text{CO}_2} = \infty$), Eq. (44) does not enter in the set of balances and four fundamental variables, $\mathbf{x} = (x_1, \dots, x_4)$, are applied

$$x_1 = \text{pMg} = -\log[\text{Mg}^{+2}], x_2 = \text{pNH}_3 = -\log[\text{NH}_3], x_3 = \text{pHPO}_4 = -\log[\text{HPO}_4^{-2}], x_4 = \text{pH} \quad (48)$$

and the sum of squares

$$SS = \sum_{i=1}^n [F_i(\mathbf{x}, \text{ppri})]^2 \quad (49)$$

is taken as the minimized (zeroed) function; $n=5$ at $C_{\text{CO}_2} > 0$ and $n=4$ at $C_{\text{CO}_2} = 0$.

At further steps of **pr1** dissolution in defined medium, the variable $\text{ppri} = -\log[\text{pri}]$, related to concentration **pr** i of the precipitate **pr** i formed in the system, was introduced against the old variable (e.g., pMg), when the solubility product K_{soi} for the precipitate **pr** i was attained; some changes in the algorithm were also made. Decision on introducing the new variable has been done on the basis of 'peering' the $\log q_i$ values (Eq.(46)). This way, one can confirm that the solid species **pr** i is (or is not) formed in the system, i.e. $\log q_i = 0$ or $\log q_i < 0$.

Generally, the calculation procedure and graphical presentation was similar to one described in the paper (Michałowski and Pietrzyk, 2006). It concerns particular species and values for the solubility or dissolution (s , mol/L) of **pr1**, expressed by the formula

$$s = [\text{Mg}^{+2}] + [\text{MgOH}^{+1}] + [\text{MgH}_2\text{PO}_4^{+1}] + [\text{MgHPO}_4] + [\text{MgPO}_4^{-1}] + [\text{MgNH}_3^{+2}] + [\text{Mg}(\text{NH}_3)_2^{+2}] + [\text{Mg}(\text{NH}_3)_3^{+2}] \quad (50)$$

at $C_{\text{CO}_2} = 0$, or

$$s' = s + [\text{MgHCO}_3^{+1}] + [\text{MgCO}_3] \quad (51)$$

at $C_{\text{CO}_2} > 0$.

12.2 The struvite dissolution – graphical presentation

The results of calculations, presented graphically in Figs. 19 – 21, are referred to two concentrations C_0 [mol/L] of **pr1**: $pC_0 = 3$ and 2 , when introduced it ($t = 0$) into aqueous solution of CO_2 (C_{CO_2} mol/L) + KOH (C_b mol/L), $C_a = 0$. Particular cases: $C_{\text{CO}_2} = 0$ and $C_b = 0$, were also considered.

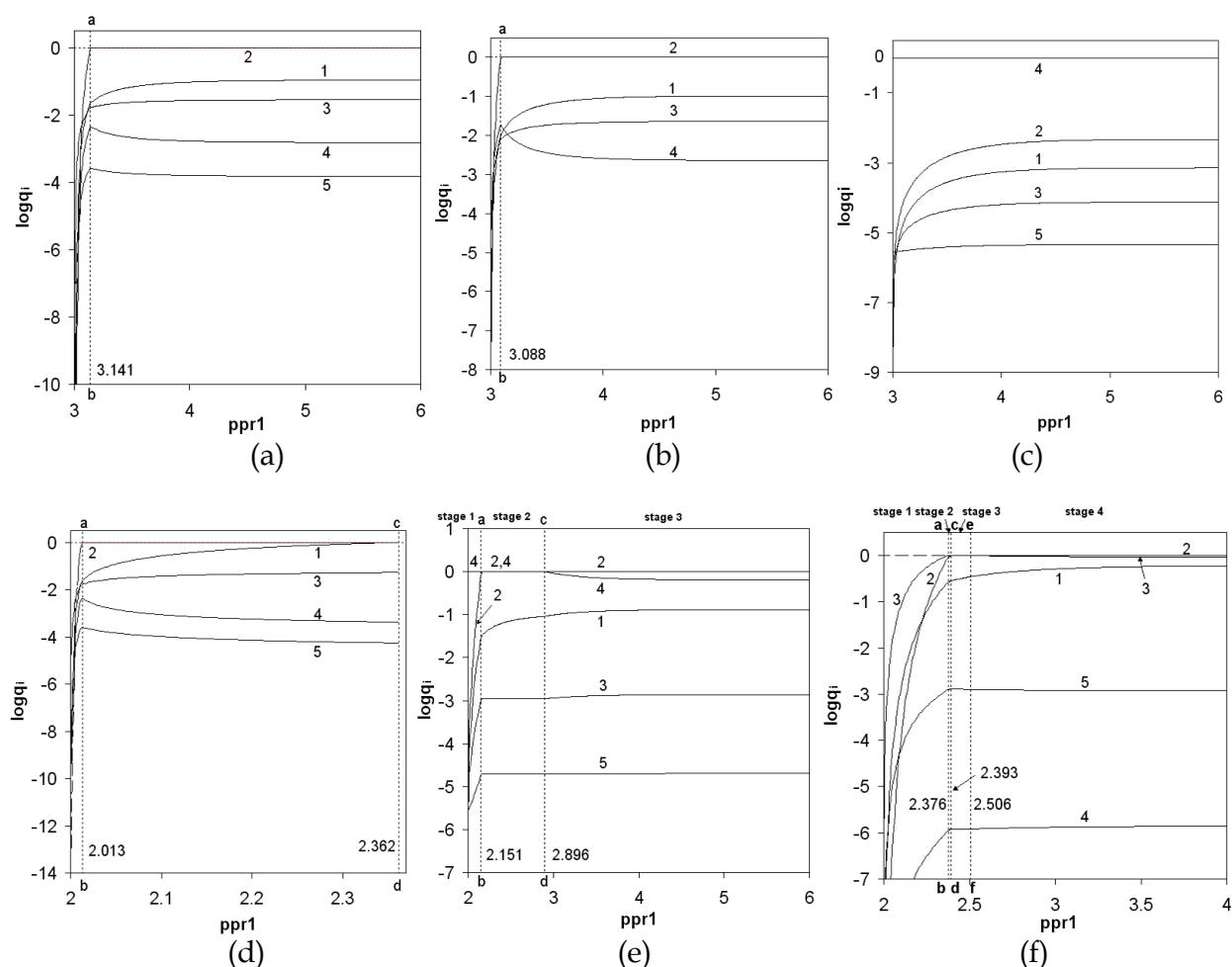


Fig. 19. The $\log q_i$ vs. ppr1 relationships for different pri ($i = 1, \dots, 5$), at different sets of $(pC_0, pC_{\text{CO}_2}, pC_b)$ values: (a) $(3, 4, \infty)$; (b) $(3, \infty, \infty)$; (c) $(3, 4, 2)$; (d) $(2, 4, \infty)$; (e) $(2, 4, 2)$; (f) $(2, 2, \infty)$.

In further parts of this chapter, two values: $C_b = 0$ and $C_b = 10^{-2}$ [mol/L] for KOH concentration will be considered. The calculations will be done for different concentrations of CO_2 , expressed by pC_{CO_2} values, equal 2, 3, 4, 5 and ∞ .

The results obtained provide the following conclusions.

At $pC_0 = 3$, $pC_{\text{CO}_2} = 4$ and $pC_b = \infty$, the solubility product K_{s02} for **pr2** is attained at $\text{ppr1} = 3.141$ (Fig. 19a), and then **pr2** is precipitated



This process lasts, up to total depletion of **pr1** (Fig.20a), i.e. the solubility product for **pr1** is not attained ($q_1 < 1$). The pH vs. **ppr1** relationship is presented in Fig. 21a. Before K_{s02} for **pr2** is attained, the values: $[\text{pr2}] = [\text{pr3}] = [\text{pr4}] = 0$ were assumed in Eqs. (40) and (42). Then, after K_{s02} attained, $[\text{pr2}]$ is introduced into (40) and (42), as the new variable. The related speciation curves are plotted in Fig.20a. The plots in Figs. 19a, 20a and 21a can be compared with ones (Figs. 19b, 20b, 21b), related to $pC_0 = 3$, $pC_{\text{CO}_2} = \infty$ and $pC_b = \infty$ (i.e. $C_{\text{CO}_2} = C_b = 0$). The course of speciation curves (Figs. 20a,20b) testifies on account of the validity of the reaction notation (52), that involves the predominating species in the system.

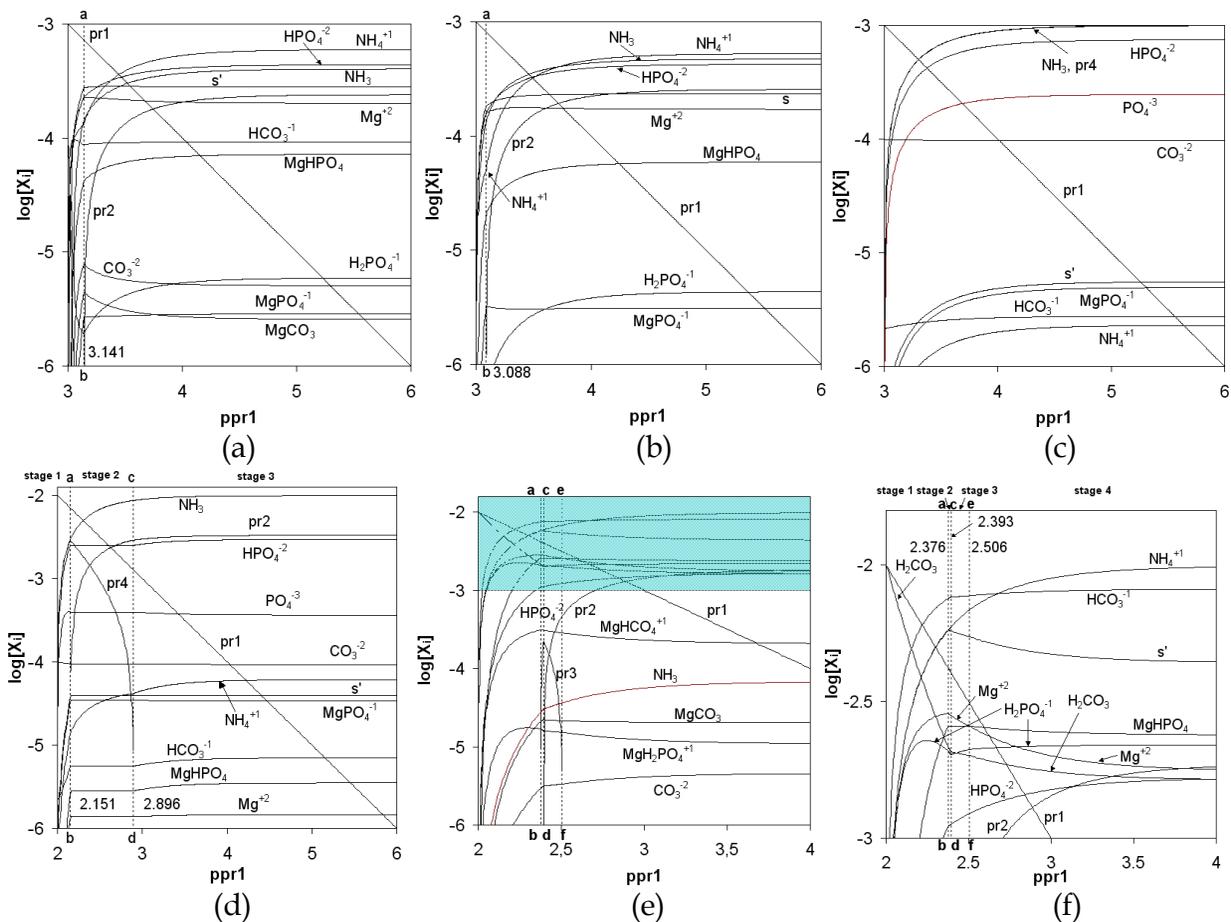


Fig. 20. The $\log[X_i]$ vs. ppr1 relationships for indicated components X_i at different sets of $(pC_0, pC_{\text{CO}_2}, pC_b)$ values: (a) (3, 4, ∞); (b) (3, ∞ , ∞); (c) (3, 4, 2); (d) (2, 4, 2); (e) (2, 2, ∞); (f) (2, 2, ∞) (detailed part of Fig. e).

At $pC_0 = 3$, $pC_{\text{CO}_2} = 4$ and $pC_b = 2$, i.e. for the case of **pr1** dissolution in alkaline media ($C_b \gg C_{\text{CO}_2}$), the **pr4** precipitates



nearly from the very start of **pr1** dissolution, $\text{ppr1} = 3.000102$ (Fig.19c,20c). The transformation of **pr1** into **pr4** lasts up to the total **pr1** depletion.

At $\text{pC}_0 = 2$, $\text{pC}_{\text{CO}_2} = 4$ and $\text{pC}_b = \infty$, the solubility product for **pr2** is attained at $\text{ppr1} = 2.013$ (Fig. 19d) and **pr2** precipitates according to reaction (52) up to $\text{ppr1} = 2.362$, where the solubility product for **pr1** is crossed and the dissolution process is terminated. At equilibrium, the solid phase consists of the two non-dissolved species **pr2** + **pr1**. The pH vs. ppr1 relationship is presented in Fig. 21c.

At $\text{pC}_0 = 2$, $\text{pC}_{\text{CO}_2} = 4$ and $\text{pC}_b = 2$, the process is more complicated and consists on three stages (Fig.19e). On the stage 1, **pr4** precipitates first (Eq. 53), nearly from the very start of **pr1** dissolution, up to $\text{ppr1} = 2.151$, where $K_{\text{so}2}$ for **pr2** is attained. Within the stage 2, the solution is saturated toward **pr2** and **pr4**. On this stage, the reaction, expressed by the notation



occurs up to total depletion of **pr4** (at $\text{ppr1} = 2.896$), see Fig.20d. On the stage 3, the reaction



occurs up to total depletion of **pr1**, i.e. solubility product ($K_{\text{so}1}$) for **pr1** is not crossed. The pH changes, occurring during this process, are presented in Fig. 21d.

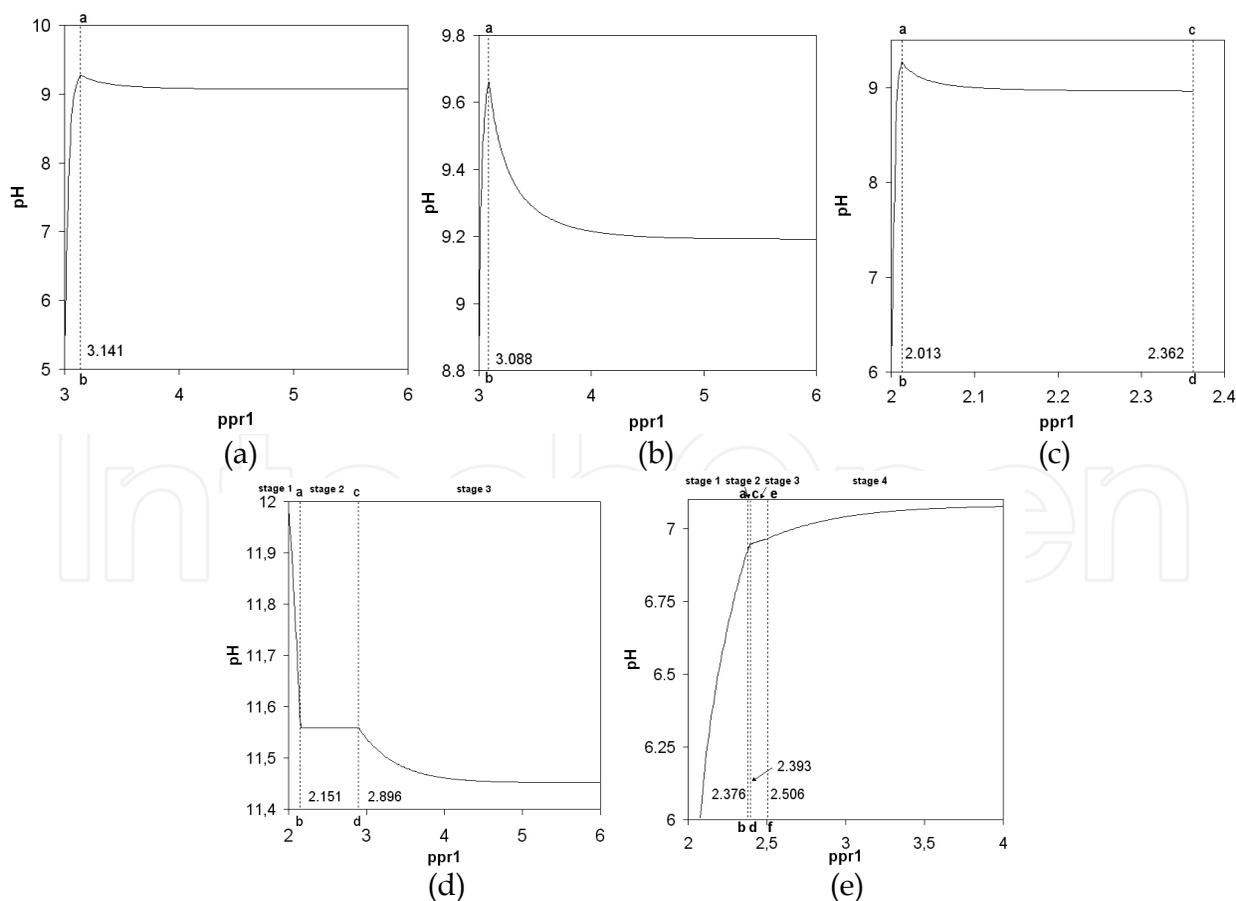


Fig. 21. The pH vs. ppr1 relationships plotted at different sets of (pC_0 , pC_{CO_2} , pC_b) values: (a) (3, 4, ∞); (b) (3, ∞ , ∞); (c) (2, 4, ∞); (d) (2, 4, 2); (e) (2, 2, ∞).

At $pC_0 = 2$, $pC_{CO_2} = 2$ and $pC_b = \infty$, after the solubility product for **pr3** attained (line ab at $ppr1 = 2.376$), **pr3** is the equilibrium solid phase up to $ppr1 = 2.393$ (line cd), where the solubility product for **pr2** is attained, see Fig.19f. For $ppr1 \in < 2.393, 2.506 >$, two equilibrium solid phases (**pr2** and **pr3**) exist in the system. Then, at $ppr1 = 2.506$, **pr3** is totally depleted (Fig.20e,2f), and then **pr1** is totally transformed into **pr2**. On particular steps, the following, predominating reactions occur:



At $ppr1 > 2.506$, only **pr2** is the equilibrium solid phase. The pH vs. $ppr1$ relationship is presented in Fig. 21e.

All the reaction equations specified above involve predominating species of the related systems. All them were formulated on the basis of the related speciation plots (Figs. 20a–20f) and confronted with the related plots of pH vs. $ppr1$ relationships. Particularly, OH^{-1} ions participate the reactions (53) and (55) as substrates and then pH of the solution decreases during the dissolution process on the stages 1 and 3 (see Fig. 21d). On the stage 2, we have $\text{pH} \cong \text{constant}$ (see Eq. 58 and Fig. 21d). A growth in concentration of NH_3 and HPO_4^{-2} is also reflected in the reactions (53) – (55) notations.

12.3 Composition of the solid phase when equimolar quantities of reagents are mixed

In this section, the solid products obtained after mixing equimolar solutions of MgCl_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ are considered at $C_{CO_2} = 0$, i.e. in absence of CO_2 . The concentrations are then equal C mol/L for magnesium, nitrogen and phosphorus ($C_{Mg} = C_N = C_P = C$). It will be stated below that the solid phase composition is also affected by the C value.

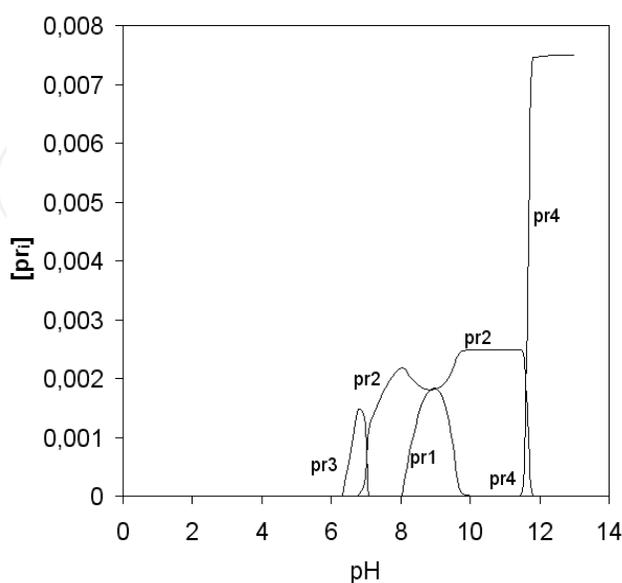


Fig. 22. The $[pri]$ vs pH plots at $C = 0.0075$ mol/L.

The relations between concentrations of different precipitates were calculated at $pK_{so1}=12.6$, $pK_{so2}=24.38$ and different C-values (0.0075, 0.02 and 0.06) assumed and presented quantitatively in Figs. 22-24. In all instances, the values: $pK_{so3} = 5.5$, $pK_{so4} = 10.74$ and all other physicochemical data cited in [1] were assumed; **pr5** is not precipitated at any instances considered in this system. Particularly, at $C = 0.0075$ it is seen that concentrations of **pr1** and **pr2** are comparable at pH ca 9.

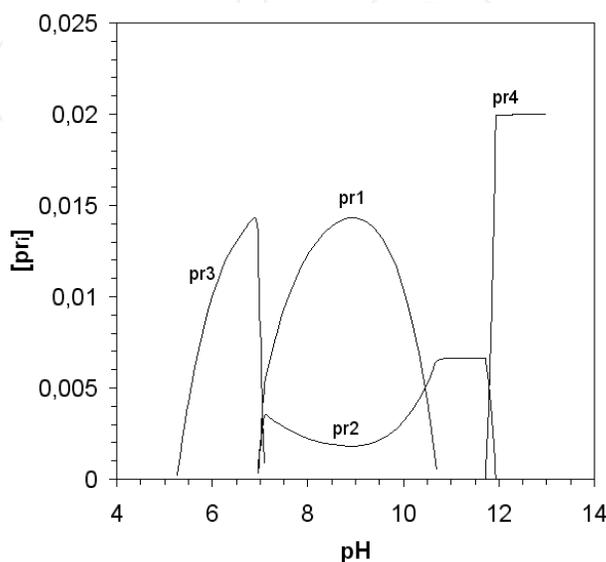


Fig. 23. The $[pri]$ vs pH plots at $C = 0.02$ mol/L.

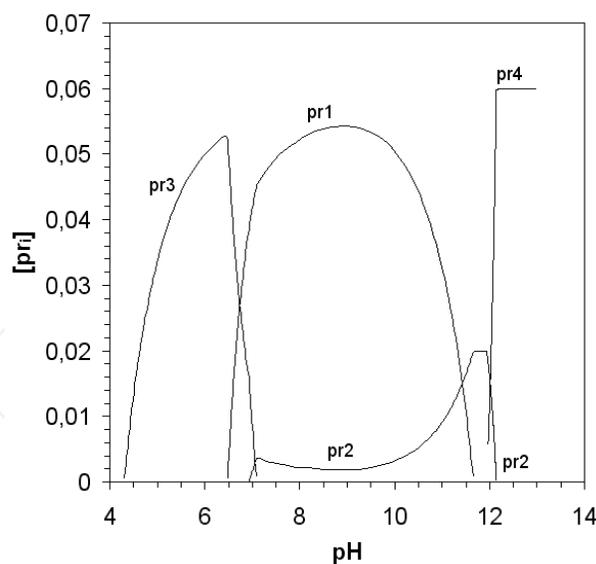


Fig. 24. The $[pri]$ vs pH plots at $C = 0.06$ mol/L.

The equilibrium constants values quoted in literature for particular species formed in the system in question are divergent. It refers, among others, to different values for pK_{so1} and pK_{so2} quoted in literature. The calculations were done on the following way.

When the solubility product (K_{soi}) for a particular precipitate (**pri**) has been crossed, the concentration $[pri]$ was involved in the related balances. At any case, the pH values

($\text{pH} \leq 13$) were related to the systems with the equilibrium solid phase(s) involved. To omit the concentration of the points referred to different Δ -values, only a part of them were plotted in the related figures (Fig. 25ab,c). Except for the data specified in Fig. 25c, where **pr1** exists as the sole solid phase within pH ca 7 – 9, irrespectively on the C -value assumed on the ordinate. In other instances, **pr1** is accompanied by **pr2**.

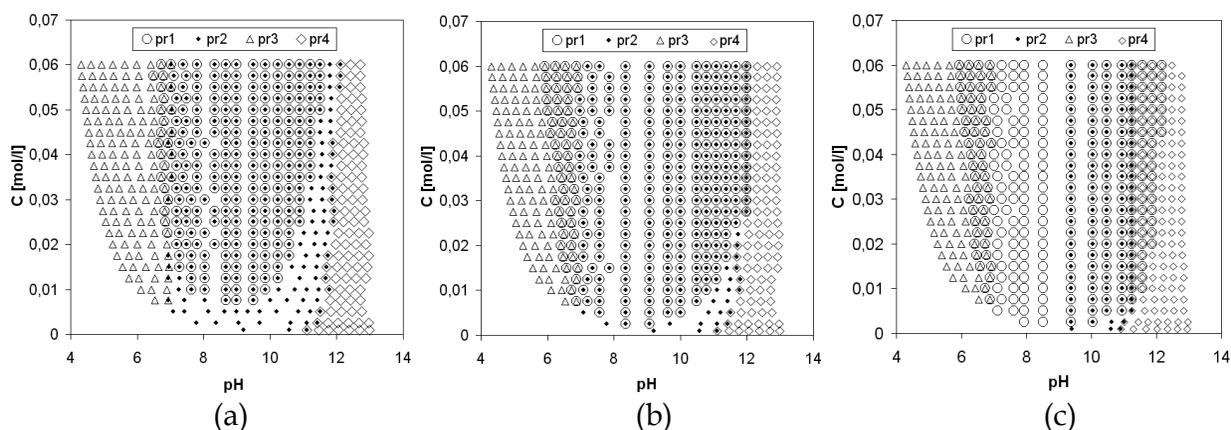


Fig. 25. The regions for indicated precipitates in (pH , C) area, calculated at different literature data for ($\text{pK}_{\text{so}1}$, $\text{pK}_{\text{so}2}$) pair: (a) (12.6, 24.38); (b) (13.15, 24.38); (c) 13.15, 23.1); $\text{pK}_{\text{sp}3} = 5.5$, $\text{pK}_{\text{so}4} = 10.74$ and other equilibrium data as ones quoted in [1].

13. A reference to kinetics in batch systems

GATES can be considered as the most general thermodynamic approach to electrolytic systems. However, one can find some reference of GATES to kinetic systems, and oscillating reactions in particular (Michałowski et al., 1996). The Belousov-Zhabotinsky (BZ) and the Bray-Liebhafsky (BL) systems, where temporal oscillations take place in continuously stirred batch reactors, are well-known examples there. Their oscillating behavior is not sufficiently known till now, as yet. The assumption of a perfect, vigorous stirring (with a stirrer or inert gas) under isothermal conditions enables the transport (diffusion) phenomena to be omitted in mathematical description of the process in question. One of the BZ oscillating systems is based on oxidation of organic components containing active methylene ($-\text{CH}_2-$) group (e.g., malonic or citric acid) with BrO_3^{-1} ions, in presence of cerium $\text{Ce}^{+4}/\text{Ce}^{+3}$ pair, in acidic (H_2SO_4) media.

To elucidate the kinetics of oscillation, exhibited by changes in potential and/or absorbance of the system, some mathematical models were applied. For example, the model known as Oregonator was usually applied for description of BZ reaction in homogeneous, perfectly mixed batch systems. Although a number of papers appear each year in chemical periodicals, an expected turning-point in generalizing approach has not set in, however (Györgyi and Field, 1992).

The oscillating reactions can proceed at constant volume and constant total concentrations of all components consisting the system (solution). It enables the related balances involved in the system to be applied. Note that radical species can also be involved within GATES, compare with Eq. (5).

All oscillating reactions known hitherto are based on electron-transfer phenomena. As a particular case, a system containing a constant, defined number of reagents mixed together,

can be considered. Thus, $s+2$ balances and their time derivatives, written in general forms (Michałowski et al., 1996):

$$\sum_j \alpha_{ij} \cdot [X_j^{z_j}] - \gamma_i = 0 \quad (60)$$

$$\sum_j \alpha_{ij} \cdot \frac{d[X_j^{z_j}]}{dt} = 0 \quad (61)$$

($i = 1, \dots, s+2$) are valid. Eqs. (60) and (61) form a set of $2(s+2)$ linearly independent equations (60), completed by linearly independent relations between concentrations of some species. All primary, intermediate and final products originated from organic substance (e.g., malonic acid) should be involved in (60) and (61), also as complexes with other ions. A due set of parameters, of both thermodynamic (e.g., standard potentials, stability constants of complexes, dissociation constants) and kinetic (rate constants) nature, are involved in there. In closed systems, with diathermal walls securing isothermal course of reactions, equations (60) and (61) are considered as (independent on time) constraints put on concentrations and rated of reactions in the system.

The time-derivatives in Eq. (61) can be expressed as follows

$$\frac{d[X_j^{z_j}]}{dt} = \sum_u k_{ju} \cdot f_u(x) - \sum_v k_{jv} \cdot f_v(x) \quad (62)$$

where k_{jw} - rate constants, $w = u, v$, $k_{jw} \geq 0$, $f_u(x)$, $f_v(x)$ - functions involving rationally selected concentrations $[X_i]$. Some species entering the balances (60), e.g., $[\text{Na}^{+1}]$ introduced by sodium bromate in BZ system, do not participate the oscillation reactions and their concentrations remain unchanged, e.g., $d[\text{Na}^{+1}]/dt = 0$.

The set of independent variables should be then formulated. For example, bromine species can be expressed by relations similar to (16), obtained on the basis of mass action law, and formulae (12). The choice of independent variables is conditioned by appropriate measuring devices applied; e.g., $[\text{Br}^{-1}]$ is measured with ion-selective bromine electrode, potential E - with platinum indicator electrode, pH - with glass electrode - all inserted with a reference electrode, in perfectly mixed cell (reactor).

Concentrations of some components cannot be directly measured with a specific, indicator electrode. In such instances, other analytical techniques must be put in work; e.g., Ce(IV) species absorb light and this property can be exploited for analytical purposes. Absorbance A , measured at wavelength λ , can be expressed by equation

$$A = \sum_j \omega_j \cdot [X_j^{z_j}] \quad (63)$$

involving the species in defined λ -range; $\omega_j = \omega_j(\lambda)$ are the coefficients defined as products of molar absorptivities, $\epsilon_j = \epsilon_j(\lambda)$, and the path length (l) of light in cuvette, $\omega_j = \epsilon_j \cdot l$. It enables any system of this kind to be resolved.

The measuring cell applied for determination of kinetic parameters should provide the possibility of simultaneous measurements of different parameters *in situ*, at different

moments of time t . The parameters considered can be found in iterative manner, through fitting the above equations to experimental data registered at different t values. Resolution of the equations and discrimination of the model may provide the temporal relationships, $y_j = y_j(t)$, namely: $[X_j] = f_j(t)$, $E = E(t)$, $\text{pH} = \text{pH}(t)$, $A = A(t)$. The relationships can be presented graphically, in 2D and 3D space.

The rudimentary formulation of balances (60) and (61) requires, among others, a deep knowledge of intermediate species formed during gradual oxidation of the organic substance (considered as the paliwo of this reaction). The experience is also needed to distinguish between the processes proceeding instantly (where equilibrium constants are only involved) and ones of kinetic nature, where rate constants are also applied.

Some limitations are caused by nature of the species formed; e.g., a limited solubility of CO_2 in BZ or O_2 in BL has to be taken into account (Gyorgyi et al., 1992).

14. Conclusions

The computer simulation realized within GATES with use of iterative computer programs, e.g., MATLAB, provides quite a new quality in knowledge gaining. It enables to follow the details of the process, registered with use of measurable quantities, such as pH and/or potential E . When referred to redox systems, it enables to gain incomparably better knowledge (Michałowski, 2010) than one offered hitherto by the well-known Pourbaix diagrams. GATES enables to avoid the necessity of quantitative 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. In calculations, the metastable state is realised by omission of potential products in the related balances, whereas 'opening' a reaction pathway in metastable state is based on insertion of possible (from equilibrium viewpoint) products in the related balances. One can also test the interference effects, of different kind.

Concentrations of the species in redox systems cover frequently much wider range of values than in non-redox systems. For example, the concentrations of oxidized forms of chloride in the system 9.2.5 are negligibly small in comparison with $[\text{Cl}^-]$; concentration of Cl_2 (the oxidized chlorine species of the highest concentration) is smaller than 10^{-14} mol/L. The concentrations of heptavalent iodine specie are lower than 10^{-20} mol/L in this system (Michałowski and Lesiak, 1994b). However, this information is not attainable *a priori*, i.e. before starting for calculations. Consideration of the generalized model before prior knowledge on the relative contents of different species, is the great advantage of GATES. The course of the plots referred to different species enables to distinguish between the main and accompanying reactions, see e.g., Figs. 6 and 7.

Some details inherent in two-phase systems cannot be tracked experimentally, with use of physicochemical or analytical instrumentation known hitherto. For example, any electrode introduced into two-phase system is the extraneous body acts as a centre of crystallisation in two-phase systems and disturbs e.g., nucleation processes occurred in such systems. Moreover, the indications of a measuring system lag behind the processes that, additionally, are based on the assumption that the process occurs uniformly within the whole system tested. The mixing device applied for this purpose is another kind of extraneous body, affecting similarly as the electrodes. Then the simulation of the dynamic processes according to GATES with use of the iterative computer program, e.g., MATLAB, involving all attainable (and pre-selected) physicochemical knowledge appears then to be the one and

only way to track them efficiently. It refers both to batch and dynamic systems, whose speciation can be followed this way.

Application of the simulating procedure (optimization *a priori*) enabled to apply some essential modifications and significant improvements of in the models applied for physicochemical and analytical needs Michałowski et al., 2008; Michałowski et al., 2011; Ponikvar et al., 2008).

According to author's experience, the main difficulties in the right description of redox systems arise on the line of junction between thermodynamics and kinetics; this line is not precisely defined in many metastable systems. One should notice that involving some species or a group of species in the balances is tantamount with 'overthrowing' the potential barrier for a reaction that is effective from thermodynamic viewpoint, but does not proceed with respect to the kinetics involved. All the inferences are based on firm, mathematical (algebraic) foundations, not on an extremely 'fragile' chemical notation principle that is only a faint imitation of a true, algebraic notation. 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, on the basis of all attainable physicochemical knowledge. Testing the complex redox and non-redox systems with use of iterative computer programs deserves wider popularisation among physico-chemists and chemists-analysts.

The generalised approach to electrolytic systems (GATES), with the generalized electron balance (GEB) concept included, is the most general theory related to thermodynamic description of equilibrium and metastable electrolytic systems, of any degree of complexity. Within GATES, all attainable/preselected physicochemical knowledge can be involved. GATES is related to non-redox and redox (batch and dynamic) systems. The GEB, results from elemental balances for H and O. Within GATES, stoichiometry is the derivative concept only.

All electrolytic systems can be reconstructed on the basis of three fundamental laws obligatory in GATES: (1) law of charge conservation, (2) conservation of elements, (3) law of mass action. Other laws known in chemistry originate from these laws. Summarizing, the GATES can be perceived as the introductory step for theory of everything (TOE) in chemistry of electrolytic systems.

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The book consists of 24 chapters illustrating a wide range of areas where MATLAB tools are applied. These areas include mathematics, physics, chemistry and chemical engineering, mechanical engineering, biological (molecular biology) and medical sciences, communication and control systems, digital signal, image and video processing, system modeling and simulation. Many interesting problems have been included throughout the book, and its contents will be beneficial for students and professionals in wide areas of interest.

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