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# Solubility Products and Solubility Concepts

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Additional information is available at the end of the chapter

**Abstract**

The chapter refers to a general concept of solubility product $K_{sp}$ of sparingly soluble hydroxides and different salts and calculation of solubility of some hydroxides, oxides, and different salts in aqueous media. A (criticized) conventional approach, based on stoichiometry of a reaction notation and the solubility product of a precipitate, is compared with the unconventional/correct approach based on charge and concentration balances and a detailed physicochemical knowledge on the system considered, and calculations realized according to generalized approach to electrolytic systems (GATES) principles. An indisputable advantage of the latter approach is proved in simulation of static or dynamic, two-phase nonredox or redox systems.

**Keywords:** electrolytic two-phase systems, solubility, dissolution, static systems, dynamic systems, computer simulation, GATES, GEB

## 1. Introduction

The problem of solubility of various chemical compounds occupies a prominent place in the scientific literature. This stems from the fact that among various properties determining the use of these compounds, the solubility is of the paramount importance. Among others, this issue has been the subject of intense activities initiated in 1979 by the Solubility Data Commission V.8 of the IUPAC Analytical Chemistry Division established and headed by S. Kertes [1], who conceived the IUPAC-NIST Solubility Data Series (SDS) project [2, 3]. Within 1979–2009, the series of 87 volumes, concerning the solubility of gases, liquids, and solids in liquids or

solids, were issued [3]; one of the volumes concerns the solubility of various oxides and hydroxides [4]. An extensive compilation of aqueous solubility data provides the Handbook of Aqueous Solubility Data [5].

*A remark*. Precipitates are marked in **bold** letters; soluble species/complexes are marked in normal letters.

The distinguishing feature of a chemical compound sparingly soluble in a particular medium is the solubility product $K_{sp}$ value. In practice, the known $K_{sp}$ values are referred only to aqueous media. One should note, however, that the expression for the solubility product and then the $K_{sp}$ value of a precipitate depend on the notation of a reaction in which this precipitate is involved. From this it follows the apparent multiplicity of $K_{sp}$'s values referred to a particular precipitate. Moreover, as will be stated below, the expression for $K_{sp}$ must not necessarily contain ionic species. On the other hand, factual or seeming lack of $K_{sp}$'s value for some precipitates is perceived; the latter issue be addressed here to $\mathbf{MnO_2}$, taken as an example.

Solubility products refer to a large group of sparingly soluble salts and hydroxides and some oxides, e.g., $\mathbf{Ag_2O}$, considered overall as hydroxides. Incidentally, other oxides, such as $\mathbf{MnO_2}$, $\mathbf{ZrO_2}$, do not belong to this group, in principle. For $\mathbf{ZrO_2}$, the solubility measurements showed quite low values even under a strongly acidic condition [6]. The solubility depends on the prior history of these oxides, e.g., prior roasting virtually eliminates the solubility of some oxides. Moderately soluble iodine ($\mathbf{I_2}$) dissolves due to reduction or oxidation, or disproportionation in alkaline media [7–12]; for $\mathbf{I_2}$, minimal solubility in water is a reference state. For 8-hydroxyquinoline, the solubility of the neutral molecule HL is a reference state; a growth in solubility is caused here by the formation of ionic species: $H_2L^{+1}$ in acidic and $L^{-1}$ in alkaline media.

The $K_{sp}$ is the main but not the only parameter used for calculation of solubility s of a precipitate. The simplifications [13] practiced in this respect are unacceptable and lead to incorrect/false results, as stated in [14–18]; more equilibrium constants are also involved with two-phase systems. These objections, formulated in the light of the generalized approach to electrolytic systems (GATES) [8], where s is the "weighed" sum of concentrations of all soluble species formed by the precipitate, are presented also in this chapter, related to nonredox and redox systems.

Calculation of s gives an information of great importance, e.g., from the viewpoint of gravimetry, where the primary step of the analysis is the quantitative transformation of a proper analyte into a sparingly soluble precipitate (salt, hydroxide). Although the precipitation and further analytical operations are usually carried out at temperatures far greater than the room temperature, at which the equilibrium constants were determined, the values of s obtained from the calculations made on the basis of equilibrium data related to room temperature are helpful in the choice of optimal *a priori* conditions of the analysis, ensuring the minimal, summary concentration of all soluble forms of the analyte, remaining in the solution, in equilibrium with the precipitate obtained after addition of an excess of the precipitating agent; this excess is referred to as relative to the stoichiometric composition of the precipitate. The ability to perform appropriate calculations, based on all available physicochemical knowledge, in accordance with the basic laws of matter conservation, deepens our knowledge of the relevant systems. At the same time, it produces the ability to acquire relevant knowledge in

an organized manner—not just imitative, but focused on heuristics. This viewpoint is in accordance with constructivist teaching, based on the belief that learning occurs, as learners are actively involved in a process of meaning and knowledge construction, as opposed to passively receiving information [19].

## 2. Definitions and formulation of solubility products

The $K_{sp}$ value refers to a two-phase system where the equilibrium solid phase is a sparingly soluble precipitate, whose $K_{sp}$ value is measured/calculated according to defined expression for the solubility product. This assumption means that the solution with defined species is saturated against this precipitate, at given temperature and composition of the solution. However, often a precipitate, when introduced into aqueous media, is not the equilibrium solid phase, and then this fundamental requirement is not complied, as indicated in examples of the physicochemical analyses of the systems with struvite $MgNH_4PO_4$ [20, 21], dolomite $CaMg(CO_3)_2$ [22, 23], and $Ag_2Cr_2O_7$.

The values of solubility products $K_{sp}$ (usually represented by solubility constant $pK_{sp} = -\log K_{sp}$ value) are known for stoichiometric precipitates of $A_aB_b$ or $A_aB_bC_c$ type, related to dissociation reactions:

$$K_{sp} = [A]^a[B]^b \text{ for } A_aB_b = aA + bB, \text{ or} \tag{1}$$

$$K_{sp} = [A]^a[B]^b[C]^c \text{ for } A_aB_bC_c = aA + bB + cC \tag{2}$$

where A and B or A, B, and C are the species forming the related precipitate; charges are omitted here, for simplicity of notation. The solubility products for more complex precipitates are unknown in the literature. The precipitates $A_aB_bC_c$ are known as ternary salts [24], e.g., struvite, dolomite, and hydroxyapatite $Ca_5(PO_4)_3OH$.

The solubility products for precipitates of $A_aB_b$ type are most frequently met in the literature. In these cases, for A are usually put simple cations of metals, or oxycations [25]; e.g., $BiO^{+1}$ and $UO_2^{+2}$ form the precipitates: $BiOCl$ and $(UO_2)_2(OH)_2$. As B, simple or more complex anions are considered, e.g., $Cl^{-1}$, $S^{-2}$, $PO_4^{-3}$, $Fe(CN)_6^{-4}$, in $AgCl$, $HgS$, $Zn_3(PO_4)_2$, and $Zn_2Fe(CN)_6$.

In different textbooks, the solubility products are usually formulated for dissociation reactions, with ions as products, also for $HgS$

$$HgS = Hg^{+2} + S^{-2} (K_{sp} = [Hg^{+2}][S^{-2}]) \tag{3}$$

although polar covalent bond exists between its constituent atoms [26]. Very low solubility product value ($pK_{sp} = 52.4$) for $HgS$ makes the dissociation according to the scheme presented by Eq. (3) impossible, and even verbal formulation of the solubility product is unreasonable. Namely, the ionic product $x = [Hg^{+2}][S^{-2}]$ calculated at $[Hg^{+2}] = [S^{-2}] = 1/N_A$ exceeds $K_{sp}$, $1/N_A^2 > K_{sp}$ ($N_A$ – Avogadro's number); the concentration $1/N_A = 1.66 \cdot 10^{-23}$ mol/L corresponds to 1 ion in 1 L of the solution. The scheme of dissociation into elemental species [14]

$$\mathbf{HgS} = \mathbf{Hg} + \mathbf{S} \ (K_{sp1} = [\mathbf{Hg}][\mathbf{S}]) \tag{4}$$

is far more favored from thermodynamic viewpoint; nonetheless, the solubility product ($K_{sp}$) for **HgS** is commonly formulated on the basis of reaction (3). We obtain $pK_{sp1} = pK_{sp} - 2A$ $(E_{01}-E_{02})$, where $E_{01} = 0.850$ V for $Hg^{+2} + 2e^{-1} = \mathbf{Hg}$, $E_{02} = -0.48$ V for $S + 2e^{-1} = S^{-2}$, $1/A = RT/F \cdot \ln 10$, $A = 16.92$ for 298 K; then $pK_{sp1} = 7.4$.

Equilibrium constants are usually formulated for the simplest reaction notations. However, in this respect, Eq. (4) is simpler than Eq. (3). Moreover, we are "accustomed" to apply solubility products with ions (cations and anions) involved, but this custom can easily be overthrown. A similar remark may concern the notation referred to elementary dissociation of mercuric iodide precipitate

$$\mathbf{HgI_2} = \mathbf{Hg} + I_2 (K_{sp1} = [\mathbf{Hg}][I_2]) \tag{5}$$
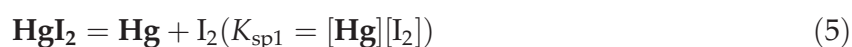
where $I_2$ denotes a soluble form of iodine in a system. From

$$\mathbf{HgI_2} = Hg^{+2} + 2I^{-1} (K_{sp} = [Hg^{+2}][I^{-1}]^2, pK_{sp} = 28.55) \tag{6}$$
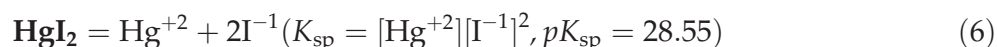
we obtain $pK_{sp1} = pK_{sp} - 2A(E_{01}-E_{03})$, where

$$E_{01} = 0.850 \text{ V for } Hg^{+2} + 2e^{-1} = \mathbf{Hg}, E_{03} = 0.621 \text{ V for } I_2 + 2e^{-1} = 2I^{-1}; \text{ then } pK_{sp1} = 20.80.$$

The species in the expression for solubility products do not predominate in real chemical systems, as a rule. However, the precipitation of **HgS** from acidified (HCl) solution of mercury salt with $H_2S$ solution can be presented in terms of predominating species; we have

$$HgCl_4^{-2} + H_2S = \mathbf{HgS} + 4Cl^{-1} + 2H^{+1} \tag{7}$$
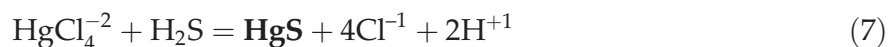
Eq. (7) can be applied to formulate the related solubility product, $K_{sp2}$, for **HgS**. To be *online* with customary requirements put on the solubility product formulation, Eq. (7) should be rewritten into the form

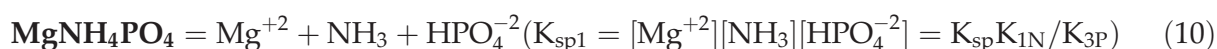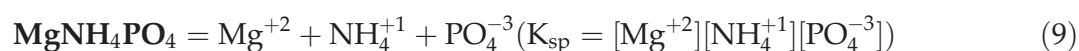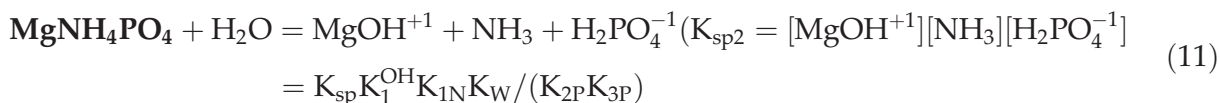$$\mathbf{HgS} + 4Cl^{-1} + 2H^{+1} = HgCl_4^{-2} + H_2S \tag{7a}$$
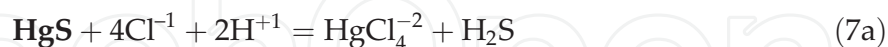
Applying the law of mass action to Eq. (7a), we have

$$K_{sp2} = \frac{[HgCl_4^{-2}][H_2S]}{[Cl^{-1}]^4[H^{+1}]^2}, \quad (pK_{sp2} = 17.33) \tag{8}$$

where $[HgCl_4^{-2}] = 10^{15.07}[Hg^{+2}][Cl^{-1}]^4$, $[H_2S] = 10^{20.0}[H^{+1}]^2[S^{-2}]$, $K_{sp}$ (Eq. (3)).

The solubility product for **MgNH₄PO₄** can be formulated on the basis of reactions:

$$\mathbf{MgNH_4PO_4} = Mg^{+2} + NH_4^{+1} + PO_4^{-3} (K_{sp} = [Mg^{+2}][NH_4^{+1}][PO_4^{-3}]) \tag{9}$$

$$\mathbf{MgNH_4PO_4} = Mg^{+2} + NH_3 + HPO_4^{-2} (K_{sp1} = [Mg^{+2}][NH_3][HPO_4^{-2}] = K_{sp}K_{1N}/K_{3P}) \tag{10}$$

$$MgNH_4PO_4 + H_2O = MgOH^{+1} + NH_3 + H_2PO_4^{-1}(K_{sp2} = [MgOH^{+1}][NH_3][H_2PO_4^{-1}]$$
$$= K_{sp}K_1^{OH}K_{1N}K_W/(K_{2P}K_{3P}) \tag{11}$$

where $K_{1N} = [H^{+1}][NH_3]/[NH_4^{+1}]$, $K_{2P} = [H^{+1}][HPO_4^{-2}]/[H_2PO_4^{-1}]$, $K_{3P} = [H^{+1}][PO_4^{-3}]/[HPO_4^{-2}]$, $[MgOH^{+1}] = K_1^{OH}[Mg^{+2}][OH^{-1}]$, $K_W = [H^{+1}][OH^{-1}]$.

Note that only uncharged (elemental) species are involved in Eqs. (4) and (5); $H_2S$ enters Eq. (8), and $NH_3$ enters Eqs. (10) and (11). This is an extension of the definition/formulation commonly met in the literature, where only charged species were involved in expression for the solubility product. Note also that small/dispersed mercury drops are neutralized with powdered sulfur, according to thermodynamically favored reaction [27]

$$Hg + S = HgS$$
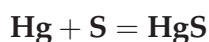
reverse to Eq. (4). Some precipitates can be optionally considered as the species of $A_aB_b$ or $A_aB_bC_c$ type. For example, the solubility product for $MgHPO_4$ can be written as $K_{sp} = [Mg^{+2}][HPO_4^{-2}]$ or $K_{sp1} = [Mg^{+2}][H^{+1}][PO_4^{-3}] = K_{sp}K_{3P}$.

The ferrocyanide ion $Fe(CN)_6^{-4}$ (with evaluated stability constant $K_6$ ca. $10^{37}$) can be considered as practically undissociated, i.e., $Fe(CN)_6^{-4}$ is kinetically inert [28], and then it does not give $Fe^{+2}$ and $CN^{-1}$ ions. The solubility product of $Zn_2Fe(CN)_6$ is $K_{sp} = [Zn^{+2}]^2[Fe(CN)_6^{-4}]$. Therefore, consideration of $Zn_2Fe(CN)_6$ as a ternary salt with $K_{sp1} = [Zn^{+2}]^2[Fe^{2+}][CN^{-1}]^6 = K_{sp}/K_6$ is not acceptable.

In principle, the solubility product values are formulated for stoichiometric compounds, and specified as such in the related tables. However, some precipitates obtained in laboratory have nonstoichiometric composition, e.g., dolomite $Ca_{1+x}Mg_{1-x}(CO_3)_2$ [22, 23], $Fe_xS$ [29]. In particular, $Fe_xS$ can be rewritten as $Fe^{+2}_pFe^{+3}_qS$; from the relations: $2p + 3q - 2 = 0$ and $p + q = x$, we get $q/p = 2(1 - x)/(3x - 2)$.

In this context, some remark needs a formulation of $K_{sp}$ for some hydroxyoxides (e.g., $FeOOH$) and oxides (e.g., $Ag_2O$). The related solubility products are formulated after completion of the corresponding reactions with water, e.g., $FeOOH + H_2O = Fe(OH)_3$, $Fe_2O_3 \cdot xH_2O + (3 - x)H_2O = 2Fe(OH)_3 \Rightarrow Fe(OH)_3 = Fe^{+3} + 3OH^{-1} \Rightarrow K_{sp} = [Fe^{+3}][OH^{-1}]^3$; $Ag_2O + H_2O = 2AgOH \Rightarrow AgOH = Ag^{+1} + OH^{-1} \Rightarrow K_{sp} = [Ag^{+1}][OH^{-1}]$, see it in the context with $gcd(a,b) = 1$.

The solubility product can be involved not only with dissociation reaction. For example, the dissolution reaction $Ca(OH)_2 + 2H^{+1} = Ca^{+2} + 2H_2O$ [30], characterized by $K_{sp1} = [Ca^{+2}]/[H^{+1}]^2$, is involved with $K_{sp} = [Ca^{+2}][OH^{-1}]^2$ in the relation $K_{sp1} = K_{sp}/K_w^2$. In Ref. [31], the solubility product is associated with formation (not dissociation) of a precipitate.
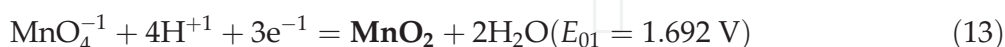
## 3. Solubility product(s) for MnO$_2$

The scheme presented above cannot be extended to all oxides. For example, one cannot recommend the formulation of this sequence for $MnO_2$, i.e., $MnO_2 + 2H_2O = Mn(OH)_4 \Rightarrow$

$\mathbf{Mn(OH)_4} = Mn^{+4} + 4OH^{-1} \Rightarrow K_{sp0} = [Mn^{+4}][OH^{-1}]^4$; $Mn^{+4}$ ions do not exist in aqueous media, and $\mathbf{MnO_2}$ is the sole Mn(+4) species present in such systems. In effect, $K_{sp0}$ for $\mathbf{MnO_2}$ is not known in the literature, compare with Ref. [32]. However, the $K_{sp}$ for $\mathbf{MnO_2}$ can be formally calculated according to an unconventional approach, based on the disproportionation reaction
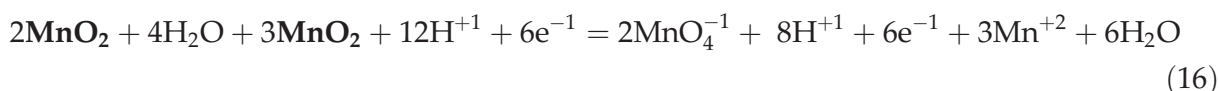
$$5\mathbf{MnO_2} + 4H^{+1} = 2MnO_4^{-1} + 3Mn^{+2} + H_2O \tag{12}$$
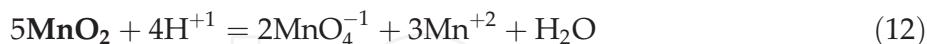
reverse to the symproportionation reaction $2MnO_4^{-1} + 3Mn^{+2} + H_2O = 5\mathbf{MnO_2} + 4H^{+1}$. The $K_{sp} = K_{sp1}$ value can be found there on the basis of $E_{01}$ and $E_{02}$ values [33], specified for reactions:

$$MnO_4^{-1} + 4H^{+1} + 3e^{-1} = \mathbf{MnO_2} + 2H_2O(E_{01} = 1.692 \text{ V}) \tag{13}$$

$$\mathbf{MnO_2} + 4H^{+1} + 2e^{-1} = Mn^{+2} + 2H_2O(E_{02} = 1.228 \text{ V}) \tag{14}$$

Eqs. (13) and (14) are characterized by the equilibrium constants:

$$K_{e1} = \frac{[MnO_2][H_2O]^2}{[MnO_4^{-1}][H^{+1}]^4[e^{-1}]^3}, \qquad K_{e2} = \frac{[Mn^{+2}][H_2O]^2}{[\mathbf{MnO_2}][H^{+1}]^4[e^{-1}]^2} \tag{15}$$

defined on the basis of mass action law (MAL) [14], where $\log K_{e1} = 3 \cdot A \cdot E_{01}$, $\log K_{e2} = 2 \cdot A \cdot E_{02}$, $A = 16.92$. From Eqs. (13) and (14), we get

$$2\mathbf{MnO_2} + 4H_2O + 3\mathbf{MnO_2} + 12H^{+1} + 6e^{-1} = 2MnO_4^{-1} + 8H^{+1} + 6e^{-1} + 3Mn^{+2} + 6H_2O \tag{16}$$

Assuming $[\mathbf{MnO_2}] = 1$ and $[H_2O] = 1$ on the stage of the $K_{sp1}$ formulation for reaction (16), equivalent to reaction (12), we have

$$K_{sp1} = \frac{[MnO_4^{-1}]^2[Mn^{+2}]^3}{[H^{+1}]^4} \tag{17}$$

and then
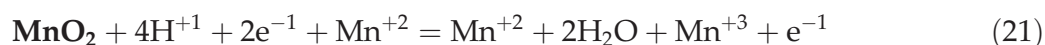
$$K_{sp1} = (K_{e2})^3 \cdot (K_{e1})^{-2} \tag{18}$$

$$pK_{sp1} = 3\log K_{e2} - 2\log K_{e1} = 6A(E_{01} - E_{02}) = 6 \cdot 16.92 \cdot (1.692 - 1.228) = 47.11 \tag{19}$$

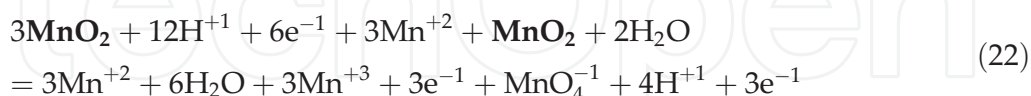The solubility products with $\mathbf{MnO_2}$ involved can be formulated on the basis of other reactions. For example, addition of
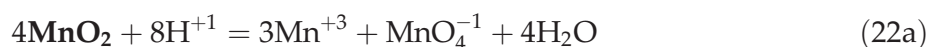
$$Mn^{+2} = Mn^{+3} + e^{-1} \tag{20}$$

to Eq. (14) gives

$$\mathbf{MnO_2} + 4H^{+1} + 2e^{-1} + Mn^{+2} = Mn^{+2} + 2H_2O + Mn^{+3} + e^{-1} \tag{21}$$

Multiplication of Eq. (21) by 3, and then addition to Eq. (13a)

$$\mathbf{MnO_2} + 2H_2O = MnO_4^{-1} + 4H^{+1} + 3e^{-1}$$

(reverse to Eq. (13)) gives the equation

$$3\mathbf{MnO_2} + 12H^{+1} + 6e^{-1} + 3Mn^{+2} + \mathbf{MnO_2} + 2H_2O$$
$$= 3Mn^{+2} + 6H_2O + 3Mn^{+3} + 3e^{-1} + MnO_4^{-1} + 4H^{+1} + 3e^{-1} \tag{22}$$

and its equivalent form, obtained after simplifications,

$$4\mathbf{MnO_2} + 8H^{+1} = 3Mn^{+3} + MnO_4^{-1} + 4H_2O \tag{22a}$$

Eq. (22) and then Eq. (22a) is characterized by the solubility product

$$K_{sp2} = \frac{[MnO_4^{-1}][Mn^{+3}]^3}{[H^{+1}]^8} = (K_{e2})^3 \cdot (K_{e3})^{-3} \cdot (K_{e1})^{-1} \tag{23}$$

where

$$K_{e3} = \frac{[Mn^{+2}]}{[Mn^{+3}][e^{-1}]} \tag{24}$$

for $Mn^{+3} + e^{-1} = Mn^{+2}$ ($E_{03}$ = 1.509 V) (reverse to Eq. (20)), $\log K_{e3} = A \cdot E_{03}$. Then

$$pK_{sp2} = 3A \cdot (E_{01} - 2E_{02} + E_{03}) + 37.82 \tag{25}$$

Formulation of $K_{spi}$ for other combinations of redox and/or nonredox reactions is also possible. This way, some derivative solubility products are obtained. The choice between the "output" and derivative solubility product values is a matter of choice. Nevertheless, one can choose the $K_{sp3}$ value related to the simplest expression for the solubility product $K_{sp3} = [Mn^{+2}][MnO_4^{-2}]$ involved with reaction $2\mathbf{MnO_2} = Mn^{+2} + MnO_4^{-2}$.

As results from calculations, the low $K_{spi}$ ($i$ = 1,2,3) values obtained from the calculations should be crossed, even in acidified solution with the related manganese species presented in **Figure 1**. In the real conditions of analysis, at $C_a$ = 1.0 mol/L, the system is homogeneous during the titration, also after crossing the equivalence point, at $\Phi = \Phi_{eq} > 0.2$; this indicates that the corresponding manganese species form a metastable system [34], unable for the symproportionation reactions.
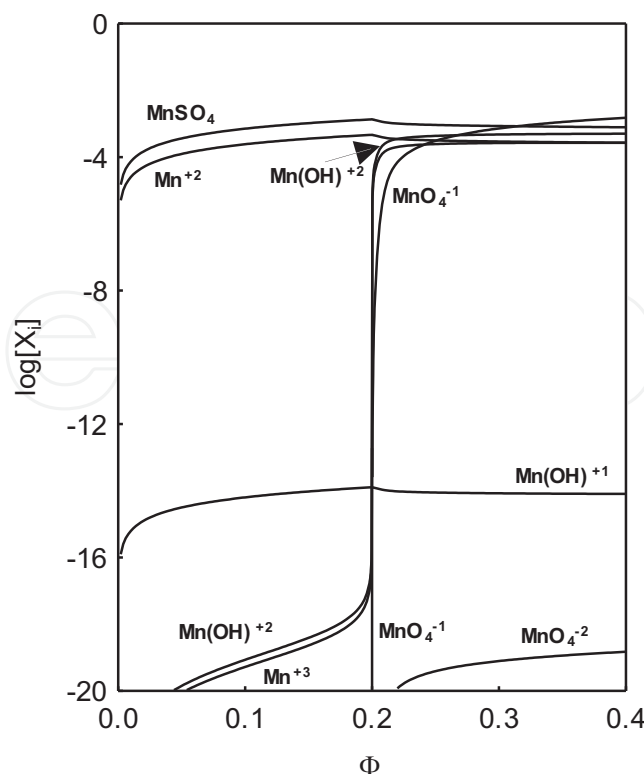
**Figure 1.** The $\log[X_i]$ versus $\Phi$ relationships for different manganese species $X_i$, plotted for titration of $V_0 = 100$ mL solution of $FeSO_4$ ($C_0 = 0.01$ mol/L) + $H_2SO_4$ ($C_a = 1.0$ mol/L) with V mL of $C = 0.02$ mol/L $KMnO_4$; $\Phi = C \cdot V/(C_0 \cdot V_0)$. The species $X_i$ are indicated at the corresponding lines.

# 4. Calculation of solubility

In this section, we compare two options applied to the subject in question. The first/criticized option, met commonly in different textbooks, is based on the stoichiometric considerations, resulting from dissociation of a precipitate, characterized by the solubility product $K_{sp}$ value, and considered *a priori* as an equilibrium solid phase in the system in question; the solubility value obtained this way will be denoted by s* [mol/L]. The second option, considered as a correct resolution of the problem, is based on full physicochemical knowledge of the system, not limited only to $K_{sp}$ value (as in the option 1); the solubility value thus obtained is denoted as s [mol/L]. The second option fulfills all requirements expressed in GATES and involved with basic laws of conservation in the systems considered. Within this option, we check, among others, whether the precipitate is really the equilibrium solid phase. The results (s*, s) obtained according to both options (1 and 2) are compared for the systems of different degree of complexity. The unquestionable advantages of GATES will be stressed this way.

## 4.1. Formulation of the solubility s*

The solubility s* will be calculated for a pure precipitate of: (1°) $A_aB_b$ or (2°) $A_aB_bC_c$ type, when introduced into pure water. Assuming $[A] = a \cdot s^*$ and $[B] = b \cdot s^*$, from Eq. (1), we have

$$s^* = \left(\frac{K_{sp}}{a^a \cdot b^b}\right)^{1/(a+b)} \tag{26}$$

and assuming $[A] = a \cdot s^*$, $[B] = b \cdot s^*$, $[C] = c \cdot s^*$, from Eq. (2), we have

$$s^* = \left(\frac{K_{sp}}{a^a \cdot b^b \cdot c^c}\right)^{1/(a+b+c)} \tag{27}$$

As a rule, the formulas (26) and (27) are invalid for different reasons, indicated in this chapter. This invalidity results, among others, from inclusion of the simplest/minor species in Eq. (26) or (27) and omission of hydroxo-complexes + other soluble complexes formed by A, and proto-complexes + other soluble complexes, formed by B. In other words, not only the species entering the expression for the related solubility product are present in the solution considered. Then the concentrations: [A], [B] or [A], [B], and [C] are usually minor species relative to the other species included in the respective balances, considered from the viewpoint of GATES [8].

## 4.2. Dissolution of hydroxides

We refer first to the simplest two-phase systems, with insoluble hydroxides as the solid phases. In all instances, $s^*$ denotes the solubility obtained from stoichiometric considerations, whereas s relates to the solubility calculated on the basis of full/attainable physicochemical knowledge related to the system in question where, except the solubility product ($K_{sp}$), other physicochemical data are also involved.

Applying formula (26) to hydroxides (B = $OH^{-1}$): **Ca(OH)$_2$** ($pK_{sp1}$ = 5.03) and **Fe(OH)$_3$** ($pK_{sp2}$ = 38.6), we have [35]

$$\mathbf{Ca(OH)_2} = Ca^{+2} + 2OH^{-1} (K_{sp1} = [Ca^{+2}][OH^{-1}]^2, \ s^* = (K_{sp1}/4)^{1/3} = 0.0133 \ \text{mol/L}) \tag{28}$$

$$\mathbf{Fe(OH)_3} = Fe^{+3} + 3OH^{-1} (K_{sp2} = [Fe^{+3}][OH^{-1}]^3, \ s^* = (K_{sp2}/27)^{1/4} = 0.98 \times 10^{-10} \text{mol/L}) \tag{29}$$

respectively. However, $Ca^{+2}$ and $Fe^{+3}$ form the related hydroxo-complexes: $[CaOH^{+1}]$ = $10^{1.3} \cdot [Ca^{+2}][OH^{-1}]$ and: $[FeOH^{+2}]$ = $10^{11.0} \cdot [Fe^{+3}][OH^{-1}]$, $[Fe(OH)_2^{+1}]$ = $10^{21.7} \cdot [Fe^{+3}][OH^{-1}]^2$; $[Fe_2(OH)_2^{+4}]$ = $10^{25.1} \cdot [Fe^{+3}]^2[OH^{-1}]^2$ [31]. The corrected expression for the solubility of **Ca(OH)$_2$** is as follows

$$s = [Ca^{+2}] + [CaOH^{+1}] \tag{30}$$

Inserting $[Ca^{+2}]$ = $K_{sp1}/[OH^{-1}]^2$ and $[OH^{-1}]$ = $K_W/[H^{+1}]$, $[H^{+1}]$ = $10^{-pH}$ ($pK_W$ = 14.0 for ionic product of water, $K_W$) into the charge balance

$$2[Ca^{+2}] + [CaOH^{+1}] + [H^{+1}] - [OH^{-1}] = 0 \qquad (31)$$

we get, by turns,

$$2 \cdot 10^{-5.03}/[OH^{-1}]^2 + 10^{1.3} \cdot 10^{-5.03}/[OH^{-1}][H^{+1}] - [OH^{-1}] = 0$$

$$\Rightarrow 2 \cdot 10^{-5.03+28-2pH} + 10^{1.3} \cdot 10^{-5.03+14-pH} + 10^{-pH} - 10^{pH-14} = 0$$

$$y(pH) = 2 \cdot 10^{22.97-2pH} + 10^{10,17-pH} + 10^{-pH} - 10^{pH-14} = 0 \qquad (32)$$

where $pH = -\log[H^{+1}]$. Applying the zeroing procedure to Eq. (30), we get $pH_0 = 12.453$ (**Table 1**), where: $[Ca^{+2}] = 0.0116$, $[CaOH^{+1}] = 0.00656$, $s = 0.0182$ mol/L (Eq. (28)). As we see, $[CaOH^{+1}]$ is comparable with $[Ca^{+2}]$, and there are none reasons to omit $[CaOH^{+1}]$ in Eq. (28).

The alkaline reaction in the system with **Ca(OH)₂** results immediately from Eq. (29): $[OH^{-1}] - [H^{+1}] = 2[Ca^{+2}] + [CaOH^{+1}] > 0$.

Analogously, for the system with **Fe(OH)₃**, we have the charge balance

$$3[Fe^{+3}] + 2[FeOH^{+2}] + [Fe(OH)_2^{+1}] + 4[Fe_2(OH)_2^{+4}] + [H^{+1}] - [OH^{-1}] = 0 \qquad (33)$$

and then

$$y(pH) = 3 \cdot 10^{3.4-3pH} + 2 \cdot 10^{0.4-2pH} + 10^{-2.9-pH} + 4 \cdot 10^{3.9-4pH} + 10^{-pH} - 10^{pH-14} = 0 \qquad (34)$$

Eq. (32) zeroes at $pH_0 = 7.0003$ (**Table 2**), where the value

$$s = [Fe^{+3}] + [FeOH^{+2}] + [Fe(OH)_2^{+1}] + 2[Fe_2(OH)_2^{+4}] \qquad (35)$$

is close to $s \cong [Fe(OH)_2^{+1}] = 10^{-9.9}$. Alkaline reaction for this system, i.e., $[OH^{-1}] > [H^{+1}]$, results immediately from Eq. (30), and $pH_0 = 7.0003$ (>7).

At pH = 7, $Fe(OH)_2^{+1}$ (not $Fe^{+3}$) is the predominating species in the system, $[Fe(OH)_2^{+1}]/[Fe^{+3}] = 10^{21.7-14} = 5 \cdot 10^7$, i.e., the equality/assumption $s^* = [Fe^{+3}]$ is extremely invalid. Moreover, the value $[OH^{-1}] = 3 \cdot s^* = 2.94 \cdot 10^{-10} = 10^{-9.532}$, i.e., pH = 4.468; this pH-value is contradictory with the inequality $[OH^{-1}] > [H^{+1}]$ resulting from Eq. (31). Similarly, extremely invalid result was

| pH | y(pH) | [OH⁻¹] | [Ca⁺²] | [CaOH⁺¹] |
|---|---|---|---|---|
| 12.451 | 0.000377 | 0.02825 | 0.01169 | 0.006592 |
| 12.452 | 0.000193 | 0.02831 | 0.01164 | 0.006577 |
| **12.453** | **8.30E-06** | **0.02838** | **0.01159** | **0.006561** |
| 12.454 | −0.000176 | 0.02844 | 0.01153 | 0.006546 |
| 12.455 | −0.000359 | 0.02851 | 0.01148 | 0.006531 |

**Table 1.** Zeroing the function (30) for the system with **Ca(OH)₂** precipitate introduced into pure water (copy of a fragment of display).

| pH | y(pH) | $[Fe^{+3}]$ | $[FeOH^{+2}]$ | $[Fe(OH)_2^{+1}]$ | $[Fe_2(OH)_2^{+4}]$ |
|---|---|---|---|---|---|
| 7.0001 | 7.99E-11 | 2.510E-18 | 2.511E-14 | 1.259E-10 | 7.936E-25 |
| 7.0002 | 3.38E-11 | 2.508E-18 | 2.510E-14 | 1.258E-10 | 7.929E-25 |
| **7.0003** | **−1.23E-11** | **2.507E-18** | **2.508E-14** | **1.258E-10** | **7.921E-25** |
| 7.0004 | −5.84E-11 | 2.505E-18 | 2.507E-14 | 1.258E-10 | 7.914E-25 |
| 7.0005 | −1.04E-10 | 2.503E-18 | 2.506E-14 | 1.257E-10 | 7.907E-25 |

**Table 2.** Zeroing the function (32) for the system with **Fe(OH)$_3$** precipitate introduced into pure water (copy of a fragment of display).

obtained in Ref. [36], where the strong hydroxo-complexes were totally omitted, and weak chloride complexes of $Fe^{+3}$ ions were included into considerations.

Taking only the main dissociating species formed in the solution saturated with respect to **Fe(OH)$_3$**, we check whether the reaction **Fe(OH)$_3$** = $Fe(OH)_2^{+1}$ + $OH^{-1}$ with $K_{sp1}$ = $[Fe(OH)_2^{+1}]$ $[OH^{-1}]$ = $10^{21.7} \cdot 10^{-38.6}$ = $10^{-16.9}$ can be used for calculation of solubility $s' = (K_{sp1})^{1/2}$ for **Fe(OH)$_3$**; the answer is also negative. Simply, the main part of $OH^{-1}$ ions originates here from dissociation of water, where the precipitate has been introduced, and then $Fe(OH)_2^{+1}$ and $OH^{-1}$ differ significantly. As we see, the diversity in $K_{sp}$ value related to a precipitate depends on its dissociation reaction notation, which disqualifies the calculation of $s^*$ based solely on the $K_{sp}$ value. This fact was not stressed in the literature issued hitherto.

Concluding, the application of the option 1, based on the stoichiometry of the reaction (29), leads not only to completely inadmissible results for $s^+$, but also to a conflict with one of the fundamental rules of conservation obligatory in electrolytic systems, namely the law of charge conservation.

Similarly, critical/disqualifying remarks can be related to the series of formulas considered in the chapter [37], e.g., $K_{sp} = 27(s^*)^4$ for precipitates of **A$_3$B** and **AB$_3$** type, and $K_{sp} = 108(s^*)^5$ for **A$_2$B$_3$** and **A$_3$B$_2$**. For **Ca$_5$(PO$_4$)$_3$OH**, the formula $K_{sp} = 84375(s^*)^9$ (!) was applied [38].

As a third example let us take a system, where an excess of **Zn(OH)$_2$** precipitate is introduced into pure water. It is usually stated that **Zn(OH)$_2$** dissociates according to the reaction

$$\mathbf{Zn(OH)_2} = Zn^{+2} + 2\,OH^{-1} \tag{36}$$

applied to formulate the expression for the solubility product

$$K_{sp3} = [Zn^{+2}][OH^{-1}]^2 (pK_{sp3} = 15.0) \tag{37}$$

The soluble hydroxo-complexes $Zn(OH)_i^{+2-i}$ (i=1,…,4), with the stability constants, $K_i^{OH}$, expressed by the values $\log K_i^{OH}$ = 4.4, 11.3, 13.14, 14.66, are also formed in the system in question. The charge balance (ChB) has the form

$$2[Zn^{+2}] + [ZnOH^{+1}] - [Zn(OH)_3^{-1}] - 2[Zn(OH)_4^{-2}] + [H^{+1}] - [OH^{-1}] = 0 \qquad (38)$$

i.e., $2 \cdot 10^{-15}/[OH^{-1}]^2 + 10^{4.4} \cdot 10^{-15}/[OH^{-1}] - 10^{13.14} \cdot 10^{-15} \cdot [OH^{-1}] - 2 \cdot 10^{14.66} \cdot 10^{-15} \cdot [OH^{-1}]^2 = 0$

$$y(pH) = 2 \cdot 10^{13-2pH} + 10^{3.4-pH} - 10^{-15.86+pH} - 2 \cdot 10^{-28.34+2pH} + 10^{-pH} - 10^{pH-14} = 0 \qquad (39)$$

The function (39) zeroes at $pH_0 = 9.121$ (see **Table 3**). The basic reaction of this system is not immediately stated from Eq. (38) (there are positive and negative terms in expression for $[OH^{-1}] - [H^{+1}]$). The solubility s value

$$s = [Zn^{+2}] + [ZnOH^{+1}] + [Zn(OH)_2] + [Zn(OH)_3^{-1}] + [Zn(OH)_4^{-2}] = 2.07 \cdot 10^{-4}$$

calculated at this point is different from $s^* = (K_{so3}/4)^{1/3} = 6.3 \cdot 10^{-6}$, and $[OH^{-1}]/[Zn^{+2}] \neq 2$; such incompatibilities contradict application of this formula.

### 4.3. Dissolution of MeL$_2$-type salts

Let us refer now to dissolution of precipitates **MeL$_2$** formed by cations Me$^{+2}$ and anions L$^{-1}$ of a strong acid HL, as presented in **Table 4**. When an excess of **MeL$_2$** is introduced into pure water, the concentration balances and charge balance in two-phase system thus formed are as follows:

| pH | $[OH^{-1}]$ | $[Zn^{+2}]$ | $[ZnOH^{+1}]$ | $[Zn(OH)_2]$ | $[Zn(OH)_3^{-1}]$ | $[Zn(OH)_4^{-2}]$ | y(pH) | s [mol/L] |
|---|---|---|---|---|---|---|---|---|
| 9.118 | 1.3122E-05 | 5.8076E-06 | 1.9143E-06 | 0.0002 | 1.8113E-07 | 7.8705E-11 | 2.2702E-07 | 0.00020743 |
| 9.119 | 1.3152E-05 | 5.7810E-06 | 1.9099E-06 | 0.0002 | 1.8155E-07 | 7.9068E-11 | 1.3858E-07 | 0.00020740 |
| 9.120 | 1.3183E-05 | 5.7544E-06 | 1.9055E-06 | 0.0002 | 1.8197E-07 | 7.9433E-11 | 5.0322E-08 | 0.00020737 |
| **9.121** | **1.3213E-05** | **5.7280E-06** | **1.9011E-06** | **0.0002** | **1.8239E-07** | **7.9800E-11** | **−3.7750E-08** | **0.00020734** |
| 9.122 | 1.3243E-05 | 5.7016E-06 | 1.8967E-06 | 0.0002 | 1.8281E-07 | 8.0168E-11 | −1.2564E-07 | 0.00020731 |
| 9.123 | 1.3274E-05 | 5.6755E-06 | 1.8923E-06 | 0.0002 | 1.8323E-07 | 8.0538E-11 | −2.1335E-07 | 0.00020728 |

**Table 3.** Zeroing the function (39) for the system with **Zn(OH)$_2$** precipitate introduced into water; $pK_W = 14$.

| Me$^{+2}$ | MeOH$^{+1}$ | Me(OH)$_2$ | Me(OH)$_3^{-1}$ | L$^{-1}$ | MeL$^{+1}$ | MeL$_2$ | MeL$_3^{-1}$ | MeL$_4^{-2}$ | MeL$_2$ |
|---|---|---|---|---|---|---|---|---|---|
| | $\log K_1^{OH}$ | $\log K_2^{OH}$ | $\log K_3^{OH}$ | | $\log K_1$ | $\log K_2$ | $\log K_3$ | $\log K_4$ | $pK_{sp}$ |
| Hg$^{+2}$ | 10.3 | 21.7 | 21.2 | I$^{-1}$ | 12.87 | 23.82 | 27.60 | 29.83 | 28.54 |
| Pb$^{+2}$ | 6.9 | 10.8 | 13.3 | I$^{-1}$ | 1.26 | 2.80 | 3.42 | 3.92 | 8.98 |
| | | | | Cl$^{-1}$ | 1.62 | 2.44 | 2.04 | 1.0 | 4.79 |

**Table 4.** $\log K_i^{OH}$ and $\log K_i$ values for the stability constants $K_i$ and $K_j$ of soluble complexes Me(OH)$_i^{+2-i}$ and MeL$_j^{+2-j}$ and $pK_{sp}$ values for the precipitates **MeL$_2$**; $[MeL_i^{+2-i}] = K_i[Me^{+2}][L^{-1}]^i$, $K_{sp} = [Me^{+2}][L^{-1}]^2$.

$$[\mathbf{MeL_2}] + [Me^{+2}] + \sum_{i=1}^{I}[Me(OH)_i^{+2-i}] + \sum_{j=1}^{J}[MeL_j^{+2-j}] = C_{Me} \qquad (40)$$

$$2[\mathbf{MeL_2}] + [L^{-1}] + \sum_{j=1}^{J}j[MeL_j^{+2-j}] = C_L \qquad (41)$$

$$[H^{+1}] - [OH^{-1}] + 2[Me^{+2}] + \sum_{i=1}^{I}(2-i)[Me(OH)_i^{+2-i}] + \sum_{j=1}^{J}(2-j)[MeL_j^{+2-j}] - [L^{-1}] = 0 \quad (42)$$

where $[\mathbf{MeL_2}]$ denotes the concentration of the precipitate $\mathbf{MeL_2}$. At $C_L = 2C_{Me}$, we have

$$2[Me^{+2}] + 2\sum_{i=1}^{I}[Me(OH)_i^{+2-i}] + \sum_{j=1}^{J}(2-j)[MeL_j^{+2-j}] = [L^{-1}] \qquad (43)$$

From Eqs. (40) and (41)

$$\alpha = [H^{+1}] - [OH^{-1}] = \sum_{i=1}^{I}i[Me(OH)_i^{+2-i}] \qquad (44)$$

i.e., reaction of the solution is acidic, $[H^{+1}] > [OH^{-1}]$. Applying the relations for the equilibrium constants:

$[Me^{+2}][L^{-1}]^2 = K_{sp}$, $[Me(OH)_i^{+2-i}] = K_i^{OH}[Me^{+2}][OH^{-1}]^i$ ($i = 1,\ldots, I$), $[MeL_j^{+2-j}] = K_j[Me^{+2}][L^{-1}]^j$ ($j = 1,\ldots, J$)

from Eqs. (43) and (44) we have

$$2[Me^{+2}]^{3/2} \cdot (1 + (1 + \sum_{i=1}^{I}x_i) + K_{sp}^{1/2} \cdot [Me^{+2}] \cdot \sum_{j=1}^{J}(2-j)K_j[L^{-1}] - K_{sp}^{1/2} = 0 \qquad (45)$$

where

$$[Me^{+2}] = \frac{\alpha}{\sum_{i=1}^{I}i \cdot x_i}; \alpha = [H^{+1}] - [OH^{-1}] = 10^{-pH} - 10^{pH-pK_W}; [L^{-1}]$$

$$= \left(\frac{K_{sp}}{[Me^{+2}]}\right)^{1/2}; x_i = K_i^{OH} \cdot (K_W/[H^{+1}])^i$$

In particular, for $I = 3$, $J = 4$ (**Table 4**), we have

$$2 \cdot \left(1 + \sum_{i=1}^{3} x_i\right) \cdot \frac{[\text{Me}]^2}{K_{\text{sp}}^{1/2}} + K_1 \cdot [\text{Me}]^{3/2} - (K_3 \cdot K_{\text{sp}} + 1) \cdot [\text{Me}]^{1/2} - 2 \cdot K_4 \cdot K_{\text{sp}}^{3/2} = 0 \qquad (46)$$

Applying the zeroing procedure to Eq. (46) gives the pH = $pH_0$ of the solution at equilibrium. At this $pH_0$ value, we calculate the concentrations of all species and solubility of this precipitate recalculated on $s_{\text{Me}}$ and $s_{\text{L}}$. When zeroing Eq. (46), we calculate pH = $pH_0$ of the solution in equilibrium with the related precipitate. The solubilities are as follows:

$$s = s_{\text{Me}} = [\text{Me}^{+2}] + \sum_{i=1}^{I} [\text{Me(OH)}_i^{+2-i}] + \sum_{j=1}^{J} [\text{MeL}_j^{+2-j}] \qquad (47)$$

$$s = s_{\text{L}} = [\text{L}^{-1}] + \sum_{j=1}^{4} j[\text{MeL}_j^{+2-j}] \qquad (48)$$

The calculations of $s_{\text{Me}}$ and $s_{\text{L}}$ for the precipitates specified in **Table 4** can be realized with use of Excel spreadsheet, according to zeroing procedure, as suggested above (**Table 1**).

For **PbI$_2$**: $pH_0$ = 5.1502, $s_{\text{Pb}}$ = 6.5276·10$^{-4}$, $s_{\text{I}}$ = 1.3051·10$^{-3}$, see **Table 6**. The difference between $s_{\text{I}}$ and $2s_{\text{Pb}}$ = 1.3055·10$^{-3}$ results from rounding the $pH_0$-value.

For **HgI$_2$**: $pH_0$ = 6.7769, $s_{\text{Hg}}$ = 1.91217·10$^{-5}$, $s_{\text{I}}$ = 3.82435·10$^{-5}$, see **Table 7**. The difference between $s_{\text{I}}$ and $2s_{\text{Hg}}$ = 3.82434·10$^{-5}$ results from rounding the pH-value. The concentration [HgI$_2$] = $K_2 K_{\text{sp}}$ = 1.90546·10$^{-5}$ is close to the $s_{\text{Hg}}$ value. For comparison, $4(s^*)^3 = K_{\text{sp}} \implies s^*$ = 1.93·10$^{-10}$, i.e., $s^*/s \approx 10^{-5}$.

| pH | [Pb$^{+2}$] | [PbOH$^{+1}$] | [Pb(OH)$_2$] | [Pb(OH)$_3^{-1}$] | [PbCl$^{+1}$] | [PbCl$_2$] | [PbCl$_3^{-1}$] | [PbCl$_4^{-2}$] | [Cl$^{-1}$] | y |
|---|---|---|---|---|---|---|---|---|---|---|
| 4.5343 | 0.010749606 | 2.92208E-05 | 7.94315E-11 | 8.59592E-18 | 0.017405892 | 0.004466836 | 6.90723E-05 | 2.44685E-07 | 0.038842191 | 0.000138249 |
| 4.5344 | 0.010744657 | 2.92141E-05 | 7.94315E-11 | 8.5979E-18 | 0.017401884 | 0.004466836 | 6.90882E-05 | 2.44798E-07 | 0.038851136 | 7.7139E-05 |
| **4.5345** | **0.01073971** | **2.92074E-05** | **7.94315E-11** | **8.59988E-18** | **0.017397878** | **0.004466836** | **6.91041E-05** | **2.44911E-07** | **0.038860083** | **1.60945E-05** |
| 4.5346 | 0.010734765 | 2.92007E-05 | 7.94315E-11 | 8.60186E-18 | 0.017393872 | 0.004466836 | 6.912E-05 | 2.45023E-07 | 0.038869032 | -4.48848E-05 |
| 4.5347 | 0.010729823 | 2.91939E-05 | 7.94315E-11 | 8.60384E-18 | 0.017389867 | 0.004466836 | 6.91359E-05 | 2.45136E-07 | 0.038877983 | -0.000105799 |

**Table 5.** Fragment of display for **PbCl$_2$**.

| pH | [Pb$^{+2}$] | [PbOH$^{+1}$] | [Pb(OH)$_2$] | [Pb(OH)$_3^{-1}$] | [PbI$^{+1}$] | [PbI$_2$] | [PbI$_3^{-1}$] | [PbI$_4^{-2}$] | [I$^{-1}$] | y |
|---|---|---|---|---|---|---|---|---|---|---|
| 5.15 | 0.000630817 | 7.07789E-06 | 7.94152E-11 | 3.54735E-17 | 1.47894E-05 | 6.60693E-07 | 3.54853E-09 | 1.44576E-11 | 0.001288393 | 0.000138249 |
| 5.1501 | 0.000630527 | 7.07626E-06 | 7.94152E-11 | 3.54816E-17 | 1.4786E-05 | 6.60693E-07 | 3.54935E-09 | 1.44643E-11 | 0.001288689 | 7.7139E-05 |
| **5.1502** | **0.000630236** | **7.07463E-06** | **7.94152E-11** | **3.54898E-17** | **1.47826E-05** | **6.60693E-07** | **3.55016E-09** | **1.44709E-11** | **0.001288986** | **1.60945E-05** |
| 5.1503 | 0.000629946 | 7.073E-06 | 7.94152E-11 | 3.5498E-17 | 1.47792E-05 | 6.60693E-07 | 3.55098E-09 | 1.44776E-11 | 0.001289283 | -4.48848E-05 |
| 5.1504 | 0.000629656 | 7.07137E-06 | 7.94152E-11 | 3.55061E-17 | 1.47758E-05 | 6.60693E-07 | 3.5518E-09 | 1.44843E-11 | 0.00128958 | -0.000105799 |

**Table 6.** Fragment of display for **PbI$_2$**.

| pH | $[Hg^{+2}]$ | $[HgOH^{+1}]$ | $[Hg(OH)_2]$ | $[Hg(OH)_3^{-1}]$ | $[HgI^{+1}]$ | $[HgI_2]$ | $[HgI_3^{-1}]$ | $[HgI_4^{-2}]$ | $[I^{-1}]$ | y |
|---|---|---|---|---|---|---|---|---|---|---|
| 6.7767 | 2.99681E-15 | 3.57569E-12 | 5.37106E-08 | 1.01569E-15 | 2.17936E-09 | 1.90546E-05 | 1.12634E-08 | 1.87646E-13 | 9.81003E-08 | 1.35932E-10 |
| 6.7768 | 2.99398E-15 | 3.57313E-12 | 5.36844E-08 | 1.01543E-15 | 2.17833E-09 | 1.90546E-05 | 1.12688E-08 | 1.87824E-13 | 9.81467E-08 | 7.72021E-11 |
| **6.7769** | **2.99114E-15** | **3.57056E-12** | **5.36583E-08** | **1.01517E-15** | **2.1773E-09** | **1.90546E-05** | **1.12741E-08** | **1.88002E-13** | **9.81932E-08** | 1.8567E-11 |
| 6.777 | 2.98831E-15 | 3.568E-12 | 5.36322E-08 | 1.0149E-15 | 2.17627E-09 | 1.90546E-05 | 1.12794E-08 | 1.88181E-13 | 9.82398E-08 | -3.99731E-11 |
| 6.7771 | 2.98548E-15 | 3.56544E-12 | 5.3606E-08 | 1.01464E-15 | 2.17524E-09 | 1.90546E-05 | 1.12848E-08 | 1.88359E-13 | 9.82863E-08 | -9.84182E-11 |

**Table 7.** Fragment of display for $HgI_2$.

## 4.4. Dissolution of $CaCO_3$ in the presence of $CO_2$

The portions 0.1 g of calcite $CaCO_3$ ($M = 100.0869$ g/mol, $d = 2.711$ g/cm$^3$) are inserted into 100 mL of: pure water (task A) or aqueous solutions of $CO_2$ specified in the tasks: B1, B2, B3, and equilibrated. Denoting the starting ($t = 0$) concentrations [mol/L]: $C^o$ for $CaCO_3$ and $C_{CO_2}$ for $CO_2$ in the related systems, on the basis of equilibrium data collected in **Table 8**:

(A) we calculate pH = $pH_{01}$ and solubility s = $s(pH_{01})$ of $CaCO_3$ at equilibrium in the system;

(B1) we calculate pH = $pH_{02}$ and solubility s = $s(pH_{02})$ of $CaCO_3$ in the system, where $C_{CO_2}$ refers to saturated (at 25 $^o$C) solution of $CO_2$, where 1.45 g $CO_2$ dissolves in 1 L of water [39].

(B2) we calculate minimal $C_{CO_2}$ in the starting solution needed for complete dissolution of $CaCO_3$ in the system and the related pH = $pH_{03}$ value, where s = $s(pH_{03}) = C^o$;

(B3) we plot the $\log s_{Ca}$ versus V, pH versus V and $\log s_{Ca}$ versus pH relationships for the system obtained after addition of V mL of a strong base MOH ($C_b = 0.1$) into $V_0 = 100$ mL of the system with $CaCO_3$ presented in (B1). The *quasistatic* course of the titration is assumed.

The volume 0.1/2.711 = 0.037 cm$^3$ of introduced $CaCO_3$ is negligible when compared with $V_0$ at the start ($t = 0$) of the dissolution. Starting concentration of $CaCO_3$ in the systems: A, B1, B2, B3 is $C^o = (0.1/100)/0.1 = 10^{-2}$ mol/L. At $t > 0$, concentration of $CaCO_3$ is c$^o$ mol/L. The balances are as follows:

| No. | Reaction | Expression for the equilibrium constant | Equilibrium data |
|---|---|---|---|
| 1 | $CaCO_3 = Ca^{+2} + CO_3^{-2}$ | $[Ca^{+2}][CO_3^{-2}] = K_{sp}$ | $pK_{sp} = 8.48$ |
| 2 | $Ca^{+2} + OH^{-1} = CaOH^{+1}$ | $[CaOH^{+1}] = K_{10}[Ca^{+2}][OH^{-1}]$ | $\log K_{10} = 1.3$ |
| 3 | $H_2CO_3 = H^{+1} + HCO_3^{-1}$ | $[H^{+1}][HCO_3^{-1}] = K_1[H_2CO_3]$ | $pK_1 = 6.38$ |
| 4 | $HCO_3^{-1} = H^{+1} + CO_3^{-2}$ | $[H^{+1}][CO_3^{-2}] = K_2[HCO_3^{-1}]$ | $pK_2 = 10.33$ |
| 5 | $Ca^{+2} + HCO_3^{-1} = CaHCO_3^{+1}$ | $[CaHCO_3^{+1}] = K_{11}[Ca^{+2}][HCO_3^{-1}]$ | $\log K_{11} = 1.11$ |
| 6 | $Ca^{+2} + CO_3^{-2} = CaCO_3$ | $[CaCO_3] = K_{12}[Ca^{+2}][CO_3^{-2}]$ | $\log K_{12} = 3.22$ |
| 7 | $Ca(OH)_2 = Ca^{+2} + 2OH^{-1}$ | $[Ca^{+2}][OH^{-1}]^2 = K_{sp1}$ | $pK_{sp1} = 5.03$ |
| 8 | $H_2O = H^{+1} + OH^{-1}$ | $[H^{+1}][OH^{-1}] = K_W$ | $pK_W = 14.0$ |

**Table 8.** Equilibrium data.

$$C^o = c^o + [Ca^{+2}] + [CaOH^{+1}] + [CaHCO_3^{+1}] + [CaCO_3] \quad \text{(for A, B1, B2, B3)} \tag{49}$$

$$C^o = c^o + [CaHCO_3^{+1}] + [CaCO_3] + [H_2CO_3] + [HCO_3^{-1}] + CO_3^{-2}] \quad \text{(for A)} \tag{50}$$

$$C^o + C_{CO2} = c^o + [CaHCO_3^{+1}] + [CaCO_3] + [H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] \text{(for B1, B2, B3)} \tag{51}$$

$$[H^{+1}] - [OH^{-1}] + 2[Ca^{+2}] + [CaOH^{+1}] + [CaHCO_3^{+1}] - [HCO_3^{-1}] - 2[CO_3^{-2}] = 0 \text{(for A, B1, B2)} \tag{52}$$

$$[H^{+1}] - [OH^{-1}] + [M^{+1}] + 2[Ca^{+2}] + [CaOH^{+1}] + [CaHCO_3^{+1}] - [HCO_3^{-1}] - 2[CO_3^{-2}] = 0 \text{(for B3)} \tag{52a}$$

where $[M^{+1}] = C_b V/(V_0 + V)$.

- For (A)

From Eqs. (49) and (50), we have

$$[Ca^{+2}] + [CaOH^{+1}] = [H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] \tag{53}$$

Considering the solution saturated with respect to **CaCO₃** and denoting: $f_1 = 10^{16.71-2pH} + 10^{10.33-pH} + 1$, $f_2 = 1 + 10^{pH-12.7}$, from Eq. (53) and **Table 1**, we have the relations:

$[Ca^{+2}]f_2 = [CO_3^{-2}] \cdot f_1 \Rightarrow [Ca^{+2}] = 10^{-4.24} \cdot (f_1/f_2)^{0.5}$; $[CO_3^{-2}] = 10^{-4.24} \cdot (f_2/f_1)^{0.5}$; $[CaOH^{+1}] = 10^{pH-16.94} \cdot (f_1/f_2)^{0.5}$;

$[CaCO_3] = 10^{-5.26}$; $[CaHCO_3^{+1}] = 10^{2.96-pH}$; $[HCO_3^{-1}] = 10^{6.09-pH} \cdot (f_2/f_1)^{0.5}$; $[H^{+1}] = 10^{-pH}$; $[OH^{-1}] = 10^{pH-14}$.

Inserting them into the charge balance (52), rewritten into the form

$$z = z(pH) = 10^{-pH} - 10^{pH-14} + 2 \cdot 10^{-4.24} \cdot (f_1/f_2)^{0.5} + 10^{pH-16.94} \cdot (f_1/f_2)^{0.5} \\ + 10^{2.96-pH} - 10^{6.09-pH} \cdot (f_2/f_1)^{0.5} - 2 \cdot 10^{-4.24} \cdot (f_2/f_1)^{0.5} \tag{54}$$

and applying the zeroing procedure to the function (54), we find $pH_{01} = 9.904$, at $z = z(pH_{01}) = 0$. The solubility s = s(pH) of **CaCO₃**, resulting from Eq. (49), is

$$s = [Ca^{+2}] + [CaOH^{+1}] + [CaHCO_3^{+1}] + [CaCO_3] \tag{55}$$

$$= 10^{-4.24} \cdot (f_1/f_2)^{0.5} + 10^{pH-16.94} \cdot (f_1/f_2)^{0.5} + 10^{2.96-pH} + 10^{-5.26} \tag{55a}$$

We have $s = s(pH = pH_{01}) = 1.159 \cdot 10^{-4}$ mol/L.

- For (B1)

Subtraction of Eq. (49) from Eq. (51) gives

$$[H_2CO_3] + [HCO_3^{-1}] + [CO_3^{-2}] - ([Ca^{+2}] + [CaOH^{+1}])$$

$$= C_{CO2} \Rightarrow [CO_3^{-2}] \cdot f_1 - [Ca^{+2}] \cdot f_2 - C_{CO2} = 0 \Rightarrow [Ca^{+2}]^2 \cdot f_2 + C_{CO2} \cdot [Ca^{+2}] - K_{sp} \cdot f_1 = 0$$

In this case,

$$[Ca^{+2}] = \frac{\sqrt{(C_{CO_2})^2 + 4 \cdot K_{sp} \cdot f_1 \cdot f_2} - C_{CO_2}}{2 \cdot f_2} \tag{56}$$

where $C_{CO_2}$ = 1.45/44 = 0.0329 mol/L. Eq. (55) has the form

$$s = [Ca^{+2}] \cdot f_2 + 10^{2.96 - pH} + 10^{-5.26} \tag{57}$$

and the charge balance is transformed into the zeroing function

$$z = z(pH) = 10^{-pH} - 10^{pH-14} + [Ca^{+2}] \cdot (2 + 10^{pH-12.7}) + 10^{2.96-pH} - [CO_3^{-2}] \cdot (10^{10.33-pH} + 2) \tag{58}$$

where $[CO_3^{-2}] = 10^{-8.48}/[Ca^{+2}]$, and $[Ca^{+2}]$ is given by Eq. (56). Eq. (58) zeroes at pH = $pH_{02}$ = 6.031. Then from Eq. (57) we calculate s = $s(pH_{02})$ = 6.393·$10^{-3}$ mol/L, at pH = $pH_{02}$ = 6.031.

- For (B2)

  At pH = $pH_{03}$, where $c^o$ = 0, i.e., s = $C^o$, the solution (a monophase system) is saturated toward **CaCO₃**, i.e., the relation $[Ca^{+2}][CO_3^{-2}] = K_{sp}$ is still valid. Applying Eqs. (56) and (57), we find pH values zeroing Eq. (58) at different, preassumed $C_{CO_2}$ values. Applying these pH-values in Eq. (57), we calculate the related s = $s(pH, C_{CO_2})$ values (Eq. (57), **Table 9**). Graphically, $C_{CO_2}$ = 0.100 is found at $pH_{03}$ = 5.683, as the abscissa of the point of intersection of the lines: s = s(pH) and s = $C^o$ = 0.01. **Table 9** shows other, preassumed s = $C^o$ values.

- For (B3)

  We apply again the formulas used in (B1) and (B2), and the charge balance (Eq. (52a)), which is transformed there into the function

| $C_{CO_2}$ | 0.090 | 0.091 | 0.092 | 0.093 | 0.094 | 0.095 | 0.096 | 0.097 | 0.098 | 0.099 | 0.100 | 0.101 | 0.102 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 5.716 | 5.712 | 5.709 | 5.706 | 5.702 | 5.699 | 5.696 | 5.693 | 5.690 | 5.687 | **5.683** | 5.680 | 5.577 |
| s | | 9.58E-3 | 9.64E-3 | 9.67E-3 | 9.70E-3 | 9.77E-3 | 9.80E-3 | 9.84E-3 | 9.87E-3 | 9.91E-3 | 9.94E-3 | **10.01E-3** | 10.06E-3 | 10.10E-3 |

**Table 9.** The set of points used for searching the $C_{CO_2}$ value at s = $C^o$ = 0.01; at this point, we have $pH_{03}$ = 5.683.
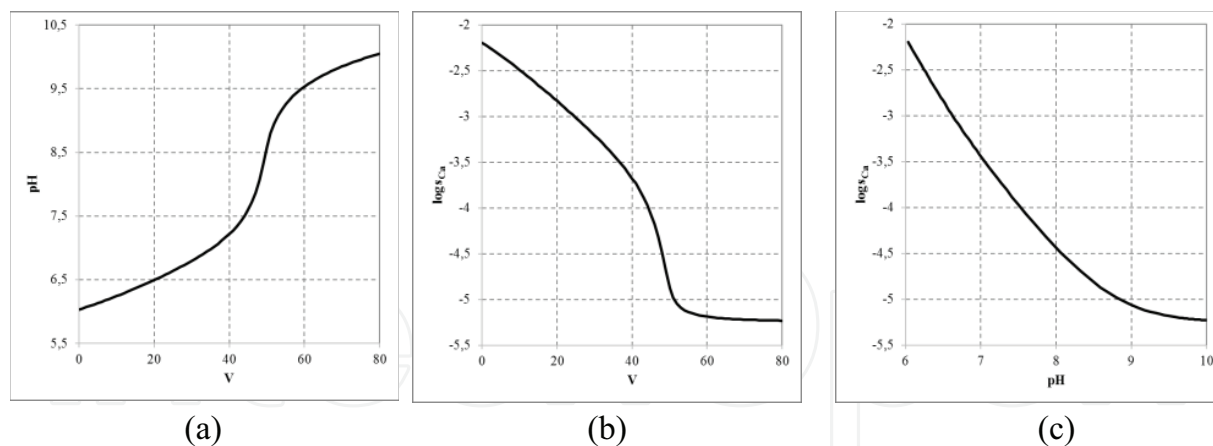
**Figure 2.** Graphical presentation of the data considered in (b3): (a) pH versus V, (b) log $s_{Ca}$ versus V, (c) log $s_{Ca}$ versus pH relationships.

$$z = z(\text{pH, V}) = 10^{-\text{pH}} - 10^{\text{pH}-14} + C_b V/(V_0 + V) + [\text{Ca}^{+2}] \cdot (2 + 10^{\text{pH}-12.7})$$
$$+ 10^{2.96-\text{pH}} - [\text{CO}_3^{-2}] \cdot (10^{10.33-\text{pH}} + 2) \tag{59}$$

applied for zeroing purposes, at different *V* values. The data thus obtained are presented graphically in Figures 2a–c. The data presented in the dynamic solubility diagram (**Figure 2**b), illustrating the solubility changes affected by pH changes (**Figure 2**a) resulting from addition of a base, MOH; **Figure 2**c shows a synthesis of these changes. Solubility product of **Ca(OH)₂** is not crossed in this system.

## 5. Nonequilibrium solid phases in aqueous media

Some solids when introduced into aqueous media (e.g., pure water) may appear to be nonequilibrium phases in these media.

### 5.1. Silver dichromate (Ag₂Cr₂O₇)

The equilibrium data related to the system, where **Ag₂Cr₂O₇** is introduced into pure water, were taken from Refs. [33, 40, 41], and presented in **Table 10**. A large discrepancy between $pK_{sp2}$ values (6.7 and 10) in the cited literature is taken here into account. We prove that **Ag₂Cr₂O₇** changes into **Ag₂CrO₄**.

On the dissociation step, each dissolving molecule of **Ag₂Cr₂O₇** gives two ions Ag⁺¹ and 1 ion Cr₂O₇⁻², where two atoms of Cr are involved; in the contact with water, these ions are hydrolyzed, to varying degrees. In the initial step of the dissolution, before the saturation of the solution with respect to an equilibrium solid phase (not specified at this moment), we can write the concentration balances

| Reaction | Equilibrium data |
|---|---|
| $H_2O = H^{+1} + OH^{-1}$ | $pK_w = 14.0$ |
| $H_2CrO_4 = H^+ + HCrO_4^{-1}$ | $pK_1 = 0.8$ |
| $HCrO_4^{-1} = H^+ + CrO_4^{-2}$ | $pK_2 = 6.5$ |
| $HCr_2O_7^{-1} = H^{+1} + Cr_2O_7^{-2}$ | $\log K_3 = 0.07$ |
| $2HCrO_4^{-1} = Cr_2O_7^{-2} + H_2O$ | $\log K_4 = 1.52$ |
| $Ag^{+1} + OH^{-1} = AgOH$ | $\log K_1^{OH} = 2.3$ |
| $Ag^{+1} + 2OH^{-1} = Ag(OH)_2^{-1}$ | $\log K_2^{OH} = 3.6$ |
| $Ag^{+1} + 3OH^{-1} = Ag(OH)_3^{-2}$ | $\log K_3^{OH} = 4.8$ |
| $\mathbf{Ag_2CrO_4} = 2Ag^{+1} + CrO_4^{-2}$ | $pK_{sp1} = 11.9$ |
| $\mathbf{Ag_2Cr_2O_7} = 2Ag^{+1} + Cr_2O_7^{-2}$ | $pK_{sp2} = 6.7$ |
| $\mathbf{AgOH} = Ag^{+1} + OH^{-1}$ | $pK_{sp3} = 7.84$ |

**Table 10.** Physicochemical equilibrium data relevant to the $\mathbf{Ag_2Cr_2O_7}$ + $H_2O$ system ($pK = -\log K$), at "room" temperatures.

$$2[\mathbf{Ag_2Cr_2O_7}] + [Ag^{+1}] + [AgOH] + [Ag(OH)_2^{-1}] + [Ag(OH)_3^{-2}] = 2C_0 \qquad (60)$$

$$2[\mathbf{Ag_2Cr_2O_7}] + [H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}] + 2[HCr_2O_7^{-1}] + 2[Cr_2O_7^{-2}] = 2C_0 \qquad (61)$$

where $2C_0$ is the total concentration of the solid phase in the system, at the moment ($t = 0$) of introducing this phase into water, $[\mathbf{Ag_2Cr_2O_7}]$ is the concentration of this phase at a given moment of the intermediary step. As previously, we assume that addition of the solid phase (here: $\mathbf{Ag_2Cr_2O_7}$) does not change the volume of the system in a significant degree, and that $\mathbf{Ag_2Cr_2O_7}$ is added in a due excess, securing the formation of a solid (that is not specified at this moment), as an equilibrium solid phase. The balances in Eqs. (60) and (61) are completed by the charge balance

$$[H^{+1}] - [OH^{-1}] + [Ag^{+1}] - [Ag(OH)_2^{-1}] - 2[Ag(OH)_3^{-2}] - [HCrO_4^{-1}]$$
$$-2[CrO_4^{-2}] - [HCr_2O_7^{-1}] - 2[Cr_2O_7^{-2}] = 0 \qquad (62)$$

used, as previously, to formulation of the zeroing function, y = y(pH), and the set of relations for equilibrium data specified in **Table 10**. From these relations, we get

$$[H_2CrO_4] = 10^{7.3-2pH} \cdot [CrO_4^{-2}]; \qquad [HCrO_4^{-1}] = 10^{6.5-pH} \cdot [CrO_4^{-2}];$$
$$[HCr_2O_7^{-1}] = 10^{14.59-3pH} \cdot [CrO_4^{-2}]^2; \qquad (63)$$

$$[Cr_2O_7^{-2}] = 10^{14.52-2pH} \cdot [CrO_4^{-2}]^2 \qquad (63a)$$

Denoting by $2c_0$ ($< 2C_0$) the total concentration of dissolved Ag and Cr species formed, in a transition stage, from $\mathbf{Ag_2Cr_2O_7}$, we can write

$$[Ag^{+1}] + [AgOH] + [Ag(OH)_2^{-1}] + [Ag(OH)_3^{-2}] = 2c_0 \tag{64}$$

$$[H_2CrO_4] + [HCrO_4^{-1}] + [CrO_4^{-2}] + 2[HCr_2O_7^{-1}] + 2[Cr_2O_7^{-2}] = 2c_0 \tag{65}$$

From **Table 10** and formulas (63)–(65) we get the relations:

$$(a) \ [Ag^{+1}] = 2c_0/g_0; \ 2g_2[CrO_4^{-2}]^2 + g_1[CrO_4^{-1}] - 2c_0 = 0 \Rightarrow (b) \ [CrO_4^{-2}] = \frac{(g_1^2 + 16 \cdot c_0 g_2)^{0.5} - g_1}{4 \cdot g_2} \tag{66}$$

where $g_0 = 1 + 10^{pH-11.7} + 10^{2pH-24.4} + 10^{3pH-37.2}$; $g_1 = 10^{7.3-2pH} + 10^{6.5-pH} + 1$; $g_2 = 10^{14.59-3pH} + 10^{14.52-2pH}$. Applying them in Eq. (62), we get the zeroing function

$$y = y(pH) = 10^{-pH} - 10^{pH-14} + g_3 \cdot [Ag^{+1}] - g_4 \cdot [CrO_4^{-2}] - g_5 \cdot [CrO_4^{-2}]^2 \tag{67}$$

where $g_3 = 1 - 10^{2pH-24.4} - 2\cdot10^{3pH-37.2}$; $g_4 = 10^{6.5-pH} + 2$; $g_5 = 10^{14.59-3pH} + 2\cdot10^{14.52-2pH}$, and $[Ag^{+1}]$ and $[CrO_4^{-2}]$ are defied above, as functions of pH.

The calculation procedure, realizable with use of Excel spreadsheet, is as follows. We assume a sequence of growing numerical values for $2c_0$. At particular $2c_0$ values, we calculate pH = pH($2c_0$) value zeroing the function (67), and then calculate the values of the products: $q_1 = [Ag^{+1}]^2[CrO_4^{-2}]/K_{sp1}$ and $q_2 = [Ag^{+1}]^2[Cr_2O_7^{-2}]/K_{sp2}$, where: $[Ag^{+1}]$, $[CrO_4^{-2}]$, and $[Cr_2O_7^{-2}]$ are presented above (Eqs. (66a), (66b) and (63a), resp.), $pK_{sp1} = 11.9$, $pK_{sp2} = 6.7$. As results from **Figure 3**, where $\log q_1$ and $\log q_2$ are plotted as functions of $2c_0$; $\log q_1 = 0 \Leftrightarrow q_1 = 1 \Leftrightarrow [Ag^{+1}]^2[CrO_4^{-2}] = K_{sp1}$ at lower $2c_0$ value, whereas $\log q_2 < 0 \Leftrightarrow q_2 < 1 \Leftrightarrow [Ag^{+1}]^2[Cr_2O_7^{-2}] < K_{sp2}$, both for $pK_2 = 6.7$ and 10, cited in the literature. The $x_1=1$
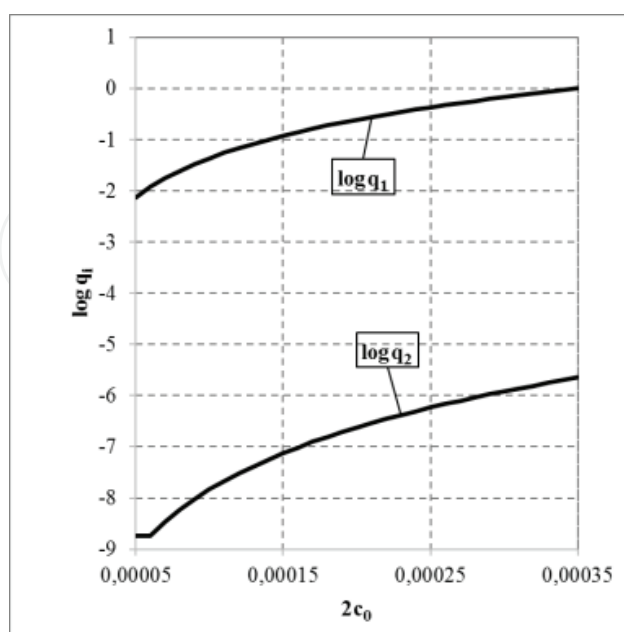


**Figure 3.** The convergence of $\log q_1$ and $\log q_2$ to 0 value; $K_{sp1}$ is attained at lower $2c_0$ value.

value is attained at $2c_0 = 3.5 \cdot 10^{-4} \implies c_0 = 1.75 \cdot 10^{-4}$; then **Ag$_2$CrO$_4$** precipitates as the new solid phase, i.e., total depletion of **Ag$_2$Cr$_2$O$_7$** occurs. It means that **Ag$_2$Cr$_2$O$_7$** is not the equilibrium solid phase in this system. This fact was confirmed experimentally, as stated in [42], i.e., **Ag$_2$Cr$_2$O$_7$** is transformed into **Ag$_2$CrO$_4$** upon boiling with H$_2$O; at higher temperatures, this transformation proceeds more effectively. Concluding, the formula s$^*$ = $(K_{sp2}/4)^{1/3}$ applied for $K_{sp2} = [Ag^{+1}]^2[Cr_2O_7^{-2}]$ is not "the best answer," as stated in Ref. [43].

The system involved with **Ag$_2$CrO$_4$** was also considered in context with the Mohr's method of Cl$^{-1}$ determination [44–46]. As were stated there, the systematic error in Cl$^{-1}$ determining according to this method, expressed by the difference between the equivalence (eq) volume ($V_{eq} = C_0V_0/C$) and the volume $V_{end}$ corresponding to the end point where the $K_{sp1}$ for **Ag$_2$CrO$_4$** is crossed, equals to

$$V_{eq} - V_{end} = \frac{K_{sp}}{C} \cdot \left(\frac{C_{01}V_0}{K_{sp1}}\right)^{0.5} \cdot (V_0 + V_{end})^{0.5} - \frac{1}{C} \cdot \left(\frac{K_{sp1}}{C_{01}V_0}\right)^{0.5} \cdot (V_0 + V_{end})^{1.5}$$

where $K_{sp} = [Ag^{+1}][Cl^{-1}]$ ($pK_{sp} = 9.75$), $V_0$ is the volume of titrant with NaCl (C$_0$) + K$_2$CrO$_4$ (C$_{01}$) titrated with AgNO$_3$ (C) solution; $V_{end} = V_{eq}$ at $C_{01} = (1 + V_{end}/V_0) \cdot K_{sp1}/K_{sp}$.

All calculations presented above were realized using Excel spreadsheets. For more complex nonequilibrium two-phase systems, the use of iterative computer programs, e.g., ones offered by MATLAB [8, 47], is required. This way, the *quasistatic* course of the relevant processes under isothermal conditions can be tested [48].

## 5.2. Dissolution of struvite

The fact that NH$_3$ evolves from the system obtained after leaving pure struvite pr1 in contact with pure water, e.g., on the stage of washing this precipitate, has already been known at the end of nineteenth century [49]. It was noted that the system obtained after mixing magnesium, ammonium, and phosphate salts at the molar ratio 1:1:1 gives a system containing an excess of ammonium species remaining in the solution and the precipitate that "*was not struvite, but was probably composed of magnesium phosphates*" [50]. This effect can be explained by the reaction [20]

$$3\mathbf{MgNH_4PO_4} = \mathbf{Mg_3(PO_4)_2} + \mathbf{HPO_4^{-2}} + \mathbf{NH_3} + 2\mathbf{NH_4^{+1}} \tag{68}$$
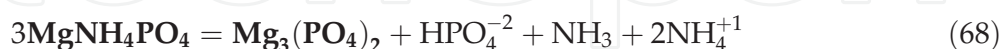
Such inferences were formulated on the basis of X-ray diffraction analysis, the crystallographic structure of the solid phase thus obtained. It was also stated that the precipitation of struvite requires a significant excess of ammonium species, e.g., Mg:N:P = 1:1.6:1. Struvite (pr1) is the equilibrium solid phase only at a due excess of one or two of the precipitating reagents. This remark is important in context with gravimetric analysis of magnesium as pyrophosphate. Nonetheless, also in recent times, the solubility of struvite is calculated from the approximate formula s$^*$ = $(K_{sp1})^{1/3}$ based on an assumption that it is the equilibrium solid phase in such a system.

Struvite is not the equilibrium solid phase also when introduced into aqueous solution of $CO_2$ ($C_{CO_2}$, mol/L), modified (or not) by free strong acid HB ($C_a$, mol/L) or strong base MOH ($C_b$, mol/L).

The case of struvite requires more detailed comments. The reaction (68) was proved theoretically [20], on the basis of simulated calculations performed by iterative computer programs, with use of all attainable physicochemical knowledge about the system in question. For this purpose, the fractions

$$q_1 = [Mg^{+2}][NH_4^{+1}][PO_4^{-3}]/K_{sp1}, q_2 = [Mg^{+2}]^3[PO_4^{-3}]^2/K_{sp2}, q_3$$
$$= [Mg^{+2}][HPO_4^{-2}]/K_{sp3}, q_4[Mg^{+2}][OH^{-1}]^2/K_{sp4}$$

(69)

were calculated for: pr1 = **MgNH₄PO₄** ($pK_{sp1}$ = 12.6), pr2 = **Mg₃(PO₄)₂** ($pK_{sp2}$ = 24.38), pr3 = **MgHPO₄** ($pK_{sp3}$ = 5.5), pr4 = **Mg(OH)₂** ($pK_{sp4}$ = 10.74) and are presented in **Figure 4**, at an initial concentration of pr1, equal $C^0 = [pr1]_{t=0} = 10^{-3}$ mol/L ($pC^0 = (ppr1)_{t=0} = 3$); ppr1 = −log [pr1]. As we see, the precipitation of pr2 (Eq. (68)) starts at ppr1 = 3.088; other solubility products are not crossed. The changes in concentrations of some species, resulting from dissolution of pr1, are indicated in **Figure 5**, where s is defined by equation [20]

$$s = s_{Mg} = [Mg^{+2}] + [MgOH^{+1}] + [MgH_2PO_4^{+1}] + [MgHPO_4] + [MgPO_4^{-1}]$$
$$+ [MgNH_3^{+2}] + [Mg(NH_3)_2^{+2}] + [Mg(NH_3)_3^{+2}]$$

(70)

involving all soluble magnesium species are identical in its form, irrespective of the equilibrium solid phase(s) present in this system. Moreover, it is stated that pH in the solution equals
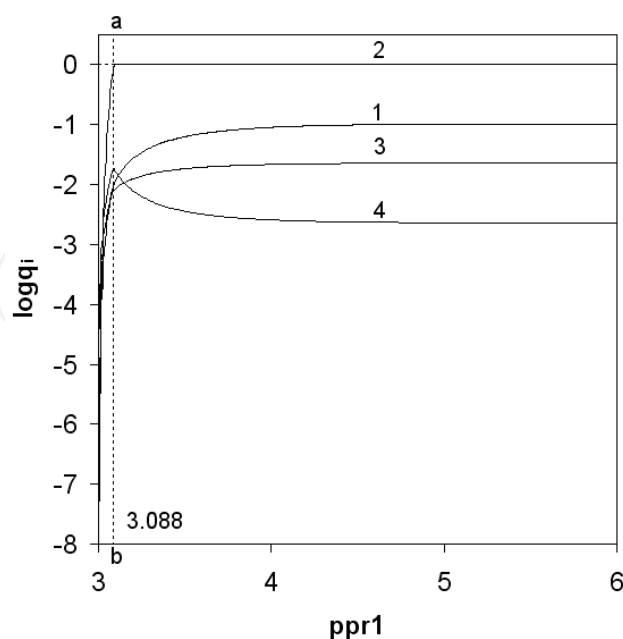


**Figure 4.** Plots of log$q_i$ versus ppr1 = −log[pr1] relationships, at (ppr1)$_{t=0}$ = 3; $i$ = 1,2,3,4 refer to pr1, pr2, pr3 and pr4, respectively.
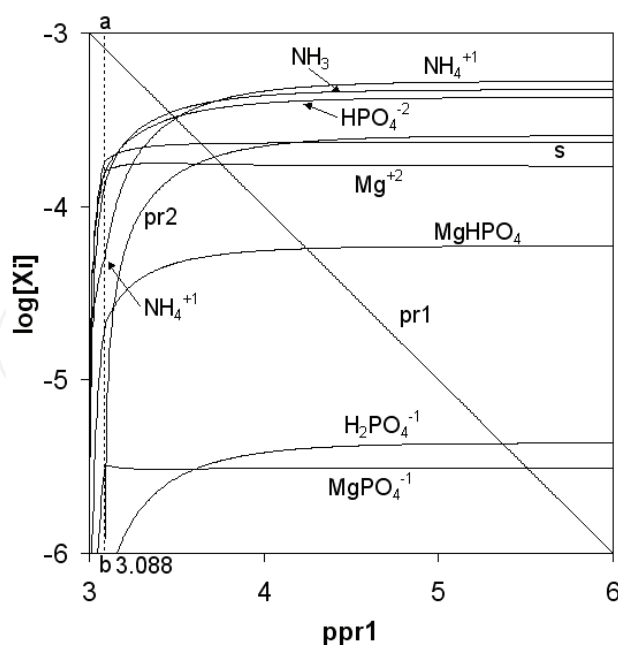
**Figure 5.** The speciation curves for indicated species resulting from dissolution of pr1 at $(ppr1)_{t=0} = 3$.

ca. 9–9.5 (**Figure 6**); this pH can be affected by the presence of $CO_2$ from air. Under such conditions, $NH_4^{+1}$ and $NH_3$ occur there at comparable concentrations $[NH_4^{+1}] \approx [NH_3]$, but $[HPO_4^{-2}]/[PO_4^{-3}] = 10^{12.36-pH} \approx 10^3$. This way, the scheme (10) would be more advantageous, provided that struvite is the equilibrium solid phase; but it is not the case, see Eq. (68). The reaction (68) occurs also in the presence of $CO_2$ in water where struvite was introduced.
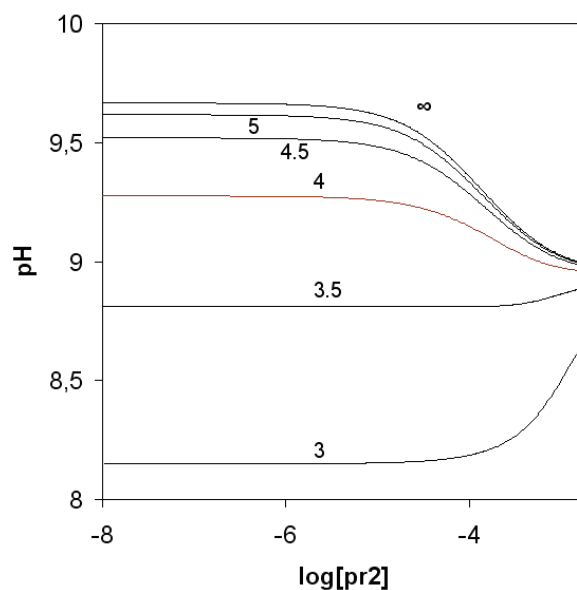


**Figure 6.** The pH versus log[pr2] relationship; pr2 = $\mathbf{Mg_3(PO_4)_2}$, at $[ppr1]_{t=0} = 3$. The numbers at the corresponding lines indicate $pCO_2 = -logC_{CO_2}$ values; $pCO_2 = \infty \Leftrightarrow C_{CO_2} = 0$.
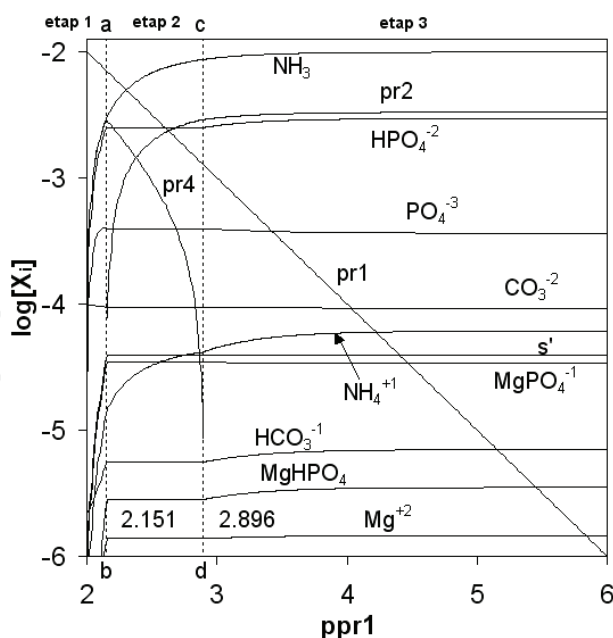
**Figure 7.** The speciation curves for indicated species $X_i^{z_i}$, resulting from dissolution of pr1 = **MgNH$_4$PO$_4$**, at (pC$_0$, pCO$_2$, pC$_b$) = (2, 4, 2); s′ is defined by Eq. (71).

After introducing struvite pr1 (at pC$_0$ = [ppr1]$_{t=0}$ = 2) into alkaline ($C_b$ = 10$^{-2}$ mol/L KOH, pC$_b$ = 2) solution of CO$_2$ (pCO$_2$ = 4), the dissolution is more complicated and proceeds in three steps, see **Figure 7**.

In step 1, pr4 precipitates first, pr1 + 2OH$^{-1}$ = pr4 + NH$_3$ + HPO$_4^{-2}$, nearly from the very start of pr1 dissolution, up to ppr1 = 2.151, where $K_{sp2}$ is attained. Within step 2, the solution is saturated toward pr2 and pr4. In this step, the reaction expressed by the notation 2pr1 + pr4 = pr2 + 2NH$_3$ + 2H$_2$O occurs up to total depletion of pr4 (at ppr1 = 2.896). In this step, the reaction 3pr1 + 2OH$^{-1}$ = pr2 + 3NH$_3$ + HPO$_4^{-1}$ + 2H$_2$O occurs up to total depletion of pr1, i.e., the solubility product $K_{sp1}$ for pr1 is not crossed. The curve s′ (**Figure 7**) is related to the function

$$s' = s + [MgHCO_3^{+1}] + [MgCO_3] \tag{71}$$

where s is expressed by Eq. (70).

## 6. Solubility of nickel dimethylglyoximate

The precipitate of nickel dimethylglyoximate, **NiL$_2$**, has soluble counterpart with the same formula, i.e., NiL$_2$, in aqueous media. If **NiL$_2$** is in equilibrium with the solution, concentration of the soluble complex NiL$_2$ assumes constant value: [NiL$_2$] = $K_2$·[Ni$^{2+}$][L$^-$]$^2$ = $K_2$·$K_{sp}$, where $K_2$ = 10$^{17.24}$, $K_{sp}$ = [Ni$^{2+}$][L$^-$]$^2$ = 10$^{-23.66}$ [14, 17, 18], and then [NiL$_2$] = 10$^{-6.42}$ (i.e., log[NiL$_2$] = −6.42). The concentration [NiL$_2$] is the constant, limiting component in expression for solubility s = s$_{Ni}$ of nickel dimethylglyoximate, **NiL$_2$**. Moreover, it is a predominant component in
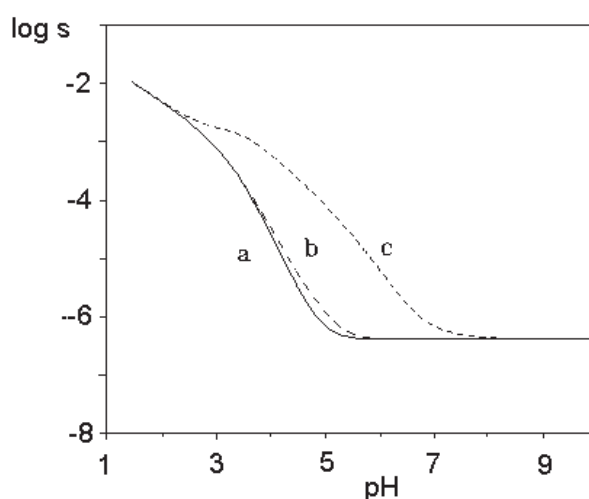
**Figure 8.** Solubility curves for nickel dimethylglyoxime **NiL₂** in (a) ammonia, (b) acetate+ammonia, and (c) citrate +acetate+ ammonia media at total concentrations [mol/L]: $C_{Ni} = 0.001$, $C_L = 0.003$, $C_N = 0.5$, $C_{Ac} = 0.3$, $C_{Cit} = 0.1$ [14].

expression for s in alkaline media, see **Figure 8**. This pH range involves pH of ammonia buffer solutions, where **NiL₂** is precipitated from $NiSO_4$ solution during the gravimetric analysis of nickel; the expression for solubility

$$s = s_{Ni} = [Ni^{+2}] + [NiOH^{+1}] + [NiSO_4] + \sum_{i=1}^{6}[Ni(NH_3)_i^{+2}] + [NiL_2] \qquad (72)$$

The effect of other, e.g., citrate (Cit) and acetate (Ac) species as complexing agents can also be considered for calculation purposes, see the lines b and c in **Figure 8**. The presence of citrate does not affect significantly the solubility of **NiL₂** in ammonia buffer media, i.e., at pH ≈ 9, where $s_{Ni} \cong [NiL_2]$.

Calculations of $s = s_{Ni}$ were made at $C_{Ni} = 0.001$ mol/L and $C_L = 0.003$ mol/L HL, i.e., at the excessive HL concentration equal $C_L - 2C_{Ni} = 0.001$ mol/L. Solubility of HL in water, equal 0.063 g HL/100 mL $H_2O$ (25°C) [51], corresponds to concentration 0.63/116.12 = 0.0054 mol/L of the saturated HL solution, 0.003 < 0.0054. Applying higher $C_L$ values needs the HL solution in ethanol, where HL is fairly soluble. However, the aqueous-ethanolic medium is thus formed, where equilibrium constants are unknown. To avoid it, lower $C_{Ni}$ and $C_L$ values were applied in calculations. The equilibrium data were taken from Ref. [31].

The soluble complex having the formula identical to the formula of the precipitate occurs also in other, two-phase systems. In some pH range, concentration of this soluble form is the dominant component of the expression for the solubility s. As stated above, such a case occurs for **NiL₂**. Then one can assume the approximation

$$s = K_2 K_{sp} \qquad (73)$$

Similar relationship exists also for other precipitates. By differentiation of Eq. (73) with respect to temperature $T$ at $p$ = const, and application of van't Hoff's isobar equation for $K_2$ and $K_{sp}$, we obtain

$$\frac{1}{s} \cdot \left(\frac{\partial s}{\partial T}\right)_p = \frac{1}{RT^2} \cdot (\Delta G_1^o + \Delta G_2^o) \tag{74}$$

where

$$\Delta G_1^o = RT^2 \cdot \left(\frac{\partial \ln K_{sp}}{\partial T}\right)_p \quad \text{and} \quad \Delta G_2^o = RT^2 \cdot \left(\frac{\partial \ln K_2}{\partial T}\right)_p$$

Because, as a rule,

$$\left(\frac{\partial K_{sp}}{\partial T}\right)_p > 0 \quad \text{and} \quad \left(\frac{\partial K_2}{\partial T}\right)_p < 0$$

then $\Delta G_1^o > 0$ and $\Delta G_2^o < 0$, and Eq. (74) can be rewritten into the form

$$\frac{1}{s} \cdot \left(\frac{\partial s}{\partial T}\right)_p = \frac{1}{RT^2} \cdot (|\Delta G_1^o| - |\Delta G_2^o|) \tag{75}$$

If $|\Delta G_1^o| \approx |\Delta G_2^o|$ within the temperature range $(T_0, T)$, the value of s is approximately constant. Let $T_0$ denote the room temperature (at which, as a rule—all the equilibrium constants are determined) and $T \neq T_0$ is the temperature at which the precipitate is filtered and washed. In this case, the solubility s and then theoretical accuracy of gravimetric analysis does not change with temperature.

## 7. Calculation of solubility in dynamic redox systems

### 7.1. Preliminary information

The redox system presented in this section is resolvable according to generalized approach to redox systems (GATES), formulated by Michałowski (1992) [8]. According to GATES principles, the algebraic balancing of any electrolytic system is based on the rules of conservation of particular elements/cores $Y_g$ ($g = 1,…, G$), and on charge balance (ChB), expressing the rule of electroneutrality of this system; the terms element and core are then distinguished. The core is a cluster of elements with defined composition (expressed by its chemical formula) and external charge that remains unchanged during the chemical process considered, e.g., titration. For ordering purposes, we assume: $Y_1 = H$, $Y_2 = O$,…. For modeling purposes, the closed systems, composed of condensed phases separated from its environment by diathermal (freely permeable by heat) walls, are considered; it enables the heat exchange between the system and its environment. Any chemical process, such as titration, is carried out under isothermal conditions, in a *quasistatic* manner; constant temperature is one of the conditions securing constancy of equilibrium constants values. An exchange of the matter ($H_2O$, $CO_2$, $O_2$,…) between the system and its environment is thus forbidden, for modeling purposes. The elemental/core balance $F(Y_g)$ for the $g$-th element/core ($Y_g$) ($g = 1,…, G$) is expressed by an equation interrelating the numbers of $Y_g$-atoms or cores in components of the system with the numbers of $Y_g$-atoms/cores in the species of the system thus formed; we have $F(H)$ for $Y_1 = H$, $F(O)$ for $Y_2 = O$, etc.

The key role in redox systems is due to generalized electron balance (GEB) concept, discovered by Michałowski as the Approach I (1992) and Approach II (2006) to GEB; both approaches are equivalent:

$$\text{Therefore, Approach II to GEB} \leftrightarrow \text{Approach I to GEB} \qquad (76)$$

GEB is fully compatible with charge balance (ChB) and concentration balances $F(Y_g)$, formulated for different elements and cores. The primary form of GEB, pr-GEB, obtained according to Approach II to GEB is the linear combination

$$\text{pr} - \text{GEB} = 2 \cdot F(O) - F(H) \qquad (77)$$

Both approaches (I and II) to GEB were widely discussed in the literature [7–12, 14, 15, 17, 18, 34, 52–74], and in three other chapters in textbooks [75–79] issued in 2017 within InTech. The GEB is perceived as a law of nature [9, 10, 17, 67, 71, 73, 74], as the hidden connection of physicochemical laws, as a breakthrough in the theory of electrolytic redox systems. The GATES refers to mono- and polyphase, redox, and nonredox, equilibrium and metastable [20, 21–23, 78, 79] static and dynamic systems, in aqueous, nonaqueous, and mixed-solvent media [69, 72], and in liquid-liquid extraction systems [53]. Summarizing, Approach II to GEB needs none prior information on oxidation numbers of all elements in components forming a redox system and in the species in the system thus formed. The Approach I to GEB, considered as the "short" version of GEB, is useful if all the oxidation numbers are known beforehand; such a case is obligatory in the system considered below. The terms "oxidant" and "reductant" are not used within both approaches. In redox systems, $2 \cdot F(O) - F(H)$ is linearly independent on CHB and $F(Y_g)$ ($g \geq 3,\ldots, G$); in nonredox systems, $2 \cdot F(O) - F(H)$ is dependent on those balances. This property distinguishes redox and nonredox systems of any degree of complexity. Within GATES, and GATES/GEB in particular, the terms: "stoichiometry," "oxidation number," "oxidant," "reductant," "equivalent mass" are considered as redundant, old-fashioned terms. The term "mass action law" (MAL) was also replaced by the equilibrium law (EL), fully compatible with the GATES principles. Within GATES, the law of charge conservation and law of conservation of all elements of the system tested have adequate importance/significance.

A detailed consideration of complex electrolytic systems requires a collection and an arrangement of qualitative (particular species) and quantitative data; the latter ones are expressed by interrelations between concentrations of the species. The interrelations consist of material balances and a complete set of expressions for equilibrium constants. Our further considerations will be referred to a titration, as a most common example of dynamic systems. The redox and nonredox systems, of any degree of complexity, can be resolved in analogous manner, without any simplifications done, with the possibility to apply all (prior, preselected) physicochemical knowledge involved in equilibrium constants related to a system in question. This way, one can simulate (imitate) the analytical prescription to any process that may be realized under isothermal conditions, in mono- and two-phase systems, with liquid-liquid extraction systems included.

## 7.2. Solubility of CuI in a dynamic redox system

The system considered in this section is related to iodometric, indirect analysis of an acidified ($H_2SO_4$) solution of $CuSO_4$ [14, 64]. It is a very interesting system, both from analytical and physicochemical viewpoints. Because the standard potential $E_0 = 0.621$ V for ($I_2$, $I^{-1}$) exceeds $E_0 = 0.153$ V for ($Cu^{+2}$, $Cu^{+1}$), one could expect (at a first sight) the oxidation of $Cu^{+1}$ by $I_2$. However, such a reaction does not occur, due to the formation of sparingly soluble **CuI** precipitate ($pK_{sp} = 11.96$).

This method consists of four steps. In the preparatory step (step 1), an excess of $H_2SO_4$ is neutralized with $NH_3$ (step 1) until a blue color appears, which is derived from $Cu(NH_3)_i^{+2}$ complexes. Then the excess of $CH_3COOH$ is added (step 2), to attain a pH ca. 3.6. After subsequent introduction of an excess of KI solution (step 3), the mixture with **CuI** precipitate and dissolved iodine formed in the reactions: $2Cu^{+2} + 4I^{-1} = 2\textbf{CuI} + I_2$, $2Cu^{+2} + 5I^{-1} = 2\textbf{CuI} + I_3^{-1}$ is titrated with $Na_2S_2O_3$ solution (step 4), until the reduction of iodine: $I_2 + 2S_2O_3^{-2} = 2I^{-1} + S_4O_6^{-2}$, $I_3^{-1} + 2S_2O_3^{-2} = 3I^{-1} + S_4O_6^{-2}$ is completed; the reactions proceed quantitatively in mildly acidic solutions (acetate buffer), where the thiosulfate species are in a metastable state. In strongly acidic media, thiosulfuric acid disproportionates according to the scheme $H_2S_2O_3 = H_2SO_3 + \textbf{S}$ [80].

## 7.3. Formulation of the system

We assume that V mL of C mol/L $Na_2S_2O_3$ solution is added into the mixture obtained after successive addition of: $V_N$ mL of $NH_3$ ($C_1$) (step 1), $V_{Ac}$ mL of $CH_3COOH$ ($C_2$) (step 2), $V_{KI}$ mL of KI ($C_3$) (step 3), and V mL of $Na_2S_2O_3$ (C) (step 4) into $V_0$ mL of titrand D composed of $CuSO_4$ ($C_0$) + $H_2SO_4$ ($C_{01}$). To follow the changes occurring in particular steps of this analysis, we assume that the corresponding reagents in particular steps are added according to the titrimetric mode, and the assumption of the volumes additivity is valid.

In this system, three electron-active elements are involved: Cu (atomic number $Z_{Cu} = 29$), I ($Z_I = 53$), S ($Z_S = 16$). Note that sulfur in the core $SO_4^{-2}$ is not involved here in electron-transfer equilibria between $S_2O_3^{-2}$ and $S_4O_6^{-2}$; then the concentration balance for sulfate species can be considered separately.

The balances written according to Approach I to GEB, in terms of molar concentrations, are as follows:
- Generalized electron balance (GEB)

$$(Z_{Cu}-2)([Cu^{+2}] + [CuOH^{+1}] + [Cu(OH)_2] + [Cu(OH)_3^{-1}] + [Cu(OH)_4^{-2}] + [CuNH_3^{+2}] + [Cu(NH_3)_2^{+2}]$$
$$+[Cu(NH_3)_3^{+2}] + [Cu(NH_3)_4^{+2}] + [CuCH_3COO^{+1}] + [Cu(CH_3COO)_2]) + (Z_{Cu} - 2 + Z_I - 5)[CuIO_3^{+1}]$$
$$+(Z_{Cu} - 1)([Cu^{+1}] + [CuNH_3^{+1}] + [Cu(NH_3)_2^{+1}]) + (Z_{Cu} + Z_I)[\textbf{CuI}_{(s)}] + (Z_{Cu} + 2Z_I + 1)[CuI_2^{-1}]$$
$$+(Z_I + 1)[I^{-1}] + (3Z_I + 1)[I_3^{-1}] + 2Z_I([I_2] + a \cdot [\textbf{I}_{2(s)}]) + (Z_I - 1)([HIO] + [IO^{-1}]) + (Z_I - 5)([HIO_3] + [IO_3^{-1}])$$
$$+(Z_I - 7)([H_5IO_6] + [H_4IO_6^{-1}] + [H_3IO_6^{-2}]) + 2 \cdot (Z_S - 2)([H_2S_2O_3] + [HS_2O_3^{-1}]) + [S_2O_3^{-2}])$$
$$+ 4 \cdot (Z_S - 2.5)[S_4O_6^{-2}] + (Z_{Cu} - 1 + 2 \cdot (Z_S - 2))[CuS_2O_3^{-1}] + (Z_{Cu} - 1 + 4 \cdot (Z_S - 2))[Cu(S_2O_3)_2^{-3}] + (Z_{Cu} - 1 + 6 \cdot (Z_S - 2))[Cu(S_2O_3)_3^{-5}] - ((Z_{Cu} - 2)C_0V_0 + (Z_I + 1)C_3V_{KI} + 2 \cdot (Z_S - 2)CV)/$$
$$(V_0 + V_N + V_{Ac} + V_{KI} + V) = 0$$

$$(78)$$

- CHB

$$[H^{+1}]–[OH^{-1}] + [K^{+1}] + [Na^{+1}] - [HSO_4^{-1}] - 2[SO_4^{-2}] + [NH_4^{+1}] - [CH_3COO^{-1}] + 2[Cu^{+2}]$$
$$+[CuOH^{+1}] - [Cu(OH)_3^{-1}]–2[Cu(OH)_4^{-2}] + 2[Cu(NH_3)^{+2}] + 2[Cu(NH_3)_3^{+2}] + 2[Cu(NH_3)_3^{+2}]$$
$$+2Cu(NH_3)_4^{+2}] + [CuCH_3COO^{+1}] - [I^{-1}] - [I_3^{-1}]–[IO^{-1}] - [IO_3^{-1}] - [H_4IO_6^{-1}] - 2[H_3IO_6^{-2}]$$
$$+[Cu^{+1}] + [CuNH_3^{+1}] + [Cu(NH_3)_2^{+1}] - [CuI_2^{-1}] + [CuIO_3^{+1}] - [HS_2O_3^{-1}] - 2[S_2O_3^{-2}]$$
$$-2[S_4O_6^{-2}] - [CuS_2O_3^{-1}] - 3[Cu(S_2O_3)_2^{-3}] - 5[Cu(S_2O_3)_3^{-5}] = 0$$

$$(79)$$

- F(Cu)

$$[Cu^{+2}] + [CuOH^{+1}] + [Cu(OH)_2] + [Cu(OH)_3^{-1}] + [Cu(OH)_4^{-2}] + [CuSO_4] + [CuNH_3^{+2}]$$
$$+[Cu(NH_3)_2^{+2}] + [Cu(NH_3)_3^{+2}] + [Cu(NH_3)_4^{+2}] + [CuCH_3COO^{+1}] + [Cu(CH_3COO)_2]$$
$$+[Cu^{+1}] + [CuNH_3^{+1}] + [Cu(NH_3)_2^{+1}] + [CuI_2^{-1}] + [\mathbf{CuI}_{(s)}] + [CuIO_3^{+1}] + [CuS_2O_3^{-1}]$$
$$+[Cu(S_2O_3)_2^{-3}] + [Cu(S_2O_3)_3^{-5}]–C_0V_0/(V_0 + V_N + V_{Ac} + V_{KI} + V) = 0$$

$$(80)$$

- F(SO_4)

$$[HSO_4^{-1}] + [SO_4^{-2}] + [CuSO_4]–C_{01}V_0/(V_0 + V_N + V_{Ac} + V_{KI} + V) = 0 \qquad (81)$$

- F(NH_3)

$$[NH_4^{+1}] + [NH_3] + [CuNH_3^{+2}] + 2[Cu(NH_3)_2^{+2}] + 3[Cu(NH_3)_3^{+2}] + 4[Cu(NH_3)_4^{+2}]$$
$$+[CuNH_3^{+1}] + 2[Cu(NH_3)_2^{+1}]–C_1V_N/(V_0 + V_N + V_{Ac} + V_{KI} + V) = 0 \qquad (82)$$

- F(CH_3COO)

$$[CH_3COOH] + [CH_3COO^{-1}] + [CuCH_3COO^{+1}] + 2[Cu(CH_3COO)_2]$$
$$–C_2V_{Ac}/(V_0 + V_N + V_{Ac} + V_{KI} + V) = 0 \qquad (83)$$

- F(K)

$$[K^{+1}] = C_3V_{KI}/(V_0 + V_N + V_{Ac} + V_{KI} + V) \qquad (84)$$

- F(I)

$$[I^{-1}] + 3[I_3^{-1}] + 2([I_2] + [\mathbf{I_2}_{(s)}]) + [HIO] + [IO^{-1}] + [HIO_3] + [IO_3^{-1}] + [H_5IO_6] + [H_4IO_6^{-1}]$$
$$+[H_3IO_6^{-2}] + 2[CuI_2^{-1}] + [\mathbf{CuI}_{(s)}] + [CuIO_3^{+1}]–C_3V_{KI}/(V_0 + V_N + V_{Ac} + V_{KI} + V) = 0$$

$$(85)$$

- F(S)

$$2[H_2S_2O_3] + 2[HS_2O_3^{-1}] + 2[S_2O_3^{-2}] + 4[S_4O_6^{-2}] + 2[CuS_2O_3^{-1}] + 4[Cu(S_2O_3)_2^{-3}]$$
$$+6[Cu(S_2O_3)_3^{-5}] - 2CV/(V_0 + V_N + V_{Ac} + V_{KI} + V) = 0 \Rightarrow [H_2S_2O_3] + [HS_2O_3^{-1}] + [S_2O_3^{-2}]$$
$$+2[S_4O_6^{-2}] + [CuS_2O_3^{-1}] + 2[Cu(S_2O_3)_2^{-3}] + 3[Cu(S_2O_3)_3^{-5}]$$
$$-CV/(V_0 + V_N + V_{Ac} + V_{KI} + V) = 0$$

$$(86)$$

- F(Na)

$$[Na^{+1}] = 2CV/(V_0 + V_N + V_{Ac} + V_{KI} + V) \qquad (87)$$

The GEB is presented here in terms of the Approach I to GEB, based on the "card game" principle, with Cu (Eq. (80)), I (Eq. (85)) as S (Eq. (86)) as "players," and H, O, S (Eq. (81)), C (from Eq. (83)), N (from Eq. (82)), K, Na as "fans." There are together 47 species involved in 2 + 6 = 8, Eqs. (78)–(83), (85), (86) and two equalities; $[K^{+1}]$ (Eq. (84)) and $[Na^{+1}]$ (Eq. (87)) are not involved in expressions for equilibrium constants, and then are perceived as numbers (not variables), at a particular $V$-value. Concentrations of the species in the equations are interrelated in 35 independent equilibrium constants:

$$[H^{+1}] = 10^{-pH}, [OH^{-1}] = 10^{pH-14}(pK_W = 14), [CuOH^{+1}] = 10^{7.0} \cdot [Cu^{+2}][OH^{-1}], [Cu(OH)_2]$$
$$= 10^{13.68} \cdot [Cu^{+2}][OH^{-1}]^2,$$
$$[Cu(OH)_3^{-1}] = 10^{17.0} \cdot [Cu^{+2}][OH^{-1}]^3, [Cu(OH)_4^{-2}] = 10^{18.5} \cdot [Cu^{+2}][OH^{-1}]^4, [CuNH_3^{+2}]$$
$$= 10^{3.39} \cdot [Cu^{+2}][NH_3],$$
$$[Cu(NH_3)_2^{+2}] = 10^{7.33} \cdot [Cu^{+2}][NH_3]^2, [Cu(NH_3)_3^{2+}] = 10^{10.06} \cdot [Cu^{+2}][NH_3]^3, [Cu(NH_3)_4^{+2}]$$
$$= 10^{12.03} \cdot [Cu^{+2}][NH_3]^4,$$
$$[CuSO_4] = 10^{2.36} \cdot [Cu^{+2}][SO_4^{-2}], [NH_4^{+1}] = 10^{9.35} \cdot [H^{+1}][NH_3], [HSO_4^{-1}] = 10^{1.8} \cdot [H^{+1}][SO_4^{-2}],$$
$$[CH_3COOH] = 10^{4.65} \cdot [H^{+1}][CH_3COO^{-1}], [Cu^{+1}][I^{-1}] = 10^{-11.96}(\text{solubitlity product for } \textbf{CuI}),$$
$$[CuI_2^{-1}] = 10^{8.85} \cdot [Cu^{+1}][I^{-1}]^2, [CuIO_3^{+1}] = 10^{0.82} \cdot [Cu^{+2}][IO_3^{-1}], [CuCH_3COO^{+1}]$$
$$= 10^{2.24} \cdot [Cu^{+2}][CH_3COO^{-1}],$$
$$[Cu(CH_3COO)_2] = 10^{3.30} \cdot [Cu^{+2}][CH_3COO^{-1}]^2, [HS_2O_3^{-1}] = 10^{1.72} \cdot [H^{+1}][S_2O_3^{-2}], [H_2S_2O_3]$$
$$= 10^{2.32} \cdot [H^{+1}]^2[S_2O_3^{-2}],$$
$$[CuS_2O_3^{-1}] = 10^{3.30} \cdot [Cu^{+1}][S_2O_3^{-2}], [Cu(S_2O_3)_2^{-3}] = 10^{12.2} \cdot [Cu^{+1}][S_2O_3^{-2}]^2, [Cu(S_2O_3)_3^{-5}]$$
$$= 10^{13.8} \cdot [Cu^{+1}][S_2O_3^{-2}]^3$$

Applying $A = 16.92$ [16], we have

$$[Cu^{+2}] = [Cu^{+1}] \cdot 10^{A(E-0.153)}; [I_2] = [I^{-1}]^2 \cdot 10^{2A(E-0.621)}, s = 1.33 \cdot 10^{-3} \text{ mol/L (solubility of } I_{2(s)}),$$

$$[I_3^{-1}] = [I^{-1}]^3 \cdot 10^{2A(E-0.545)}, [IO^{-1}] = [I^-] \cdot 10^{2A(E-0.49)+2pH-28}, [HIO] = 10^{10.6} \cdot [H^{+1}][IO^{-1}], [IO_3^{-1}]$$

$$= [I^{-1}] \cdot 10^{6A(E-1.08)+6pH},$$

$$[HIO_3] = 10^{0.79} \cdot [H^{+1}][IO_3^{-1}], [H_5IO_6] = [I^{-1}] \cdot 10^{8A(E-1.24)+7pH}, [H_4IO_6^{-1}]$$

$$= [H_5IO_6] \cdot 10^{-3.3+pH}, [H_3IO_6^{-2}] = [I^{-1}] \cdot 10^{8A(E-0.37)+9pH-126}.$$

In the calculations made in this system according to the computer programs attached to Ref. [64], it was assumed that $V_0 = 100$, $C_0 = 0.01$, $C_{01} = 0.01$, $C_1 = 0.25$, $C_2 = 0.75$, $C_3 = 2.0$, $C_4 = C = 0.1$; $V_N = 20$, $V_{Ac} = 40$, $V_K = 20$. At each stage, the variable $V$ is considered as a volume of the solution added, consecutively: $NH_3$, $CH_3COOH$, $KI$, and $Na_2S_2O_3$, although the true/factual titrant in this method is the $Na_2S_2O_3$ solution, added in stage 4.

The solubility s [mol/L] of **CuI** in this system (**Figures 8a** and **b**) is put in context with the speciation diagrams presented in **Figure 9**. This precipitate appears in the initial part of titration with KI ($C_3$) solution (**Figure 8a**) and further it accompanies the titration, also in stage 4 (**Figure 8b**). Within stage 3, at $V \geq C_0V_0/C_3$, we have

$$s = s_3 = [Cu^{+2}] + \sum_{i=1}^{4}[Cu(OH)_i^{+2-i}] + \sum_{i=1}^{4}[Cu(NH_3)_i^{+2}] + [CuSO_4] + [CuIO_3^{+1}]$$

$$+ \sum_{i=1}^{2}[Cu(CH_3COO)_i^{+2-i}] + [Cu^{+1}] + [CuI_2^{-1}] + \sum_{i=1}^{2}[Cu(NH_3)_i^{+1}] \tag{88}$$

and in stage 4

$$s = s_4 = s_3 + \sum_{i=1}^{3}[Cu(S_2O_3)_i^{+1-2i}] \tag{89}$$

The small concentration of $Cu^{+1}$ (**Figure 9**, stage 3) occurs at a relatively high total concentration of $Cu^{+2}$ species, determining the potential ca. 0.53–0.58 V, $[Cu^{+2}]/[Cu^{+1}] = 10^{A(E-0.153)}$, see **Figure 10a**. Therefore, the concentration of $Cu^{+2}$ species determine a relatively high solubility s in the initial part of stage 3. The decrease in the s value in further parts of stage 3 is continued in stage 4, at $V < V_{eq} = C_0V_0/C = 0.01 \cdot 100/0.1 = 10$ mL. Next, a growth in the solubility $s_4$ at $V > V_{eq}$ is involved with formation of thiosulfate complexes, mainly $CuS_2O_3^{-1}$ (**Figure 9**, stage 4). The species $I_3^{-1}$ and $I_2$ are consumed during the titration in stage 4 (**Figure 9d**). A sharp drop of $E$ value at $V_{eq} = 10$ mL (**Figure 10b**) corresponds to the fraction titrated $\Phi_{eq} = 1$.

The course of the $E$ versus $V$ relationship within the stage 3 is worth mentioning (**Figure 10a**). The corresponding curve initially decreases and reaches a "sharp" minimum at the point corresponding to crossing the solubility product for **CuI**. Precipitation of **CuI** starts after
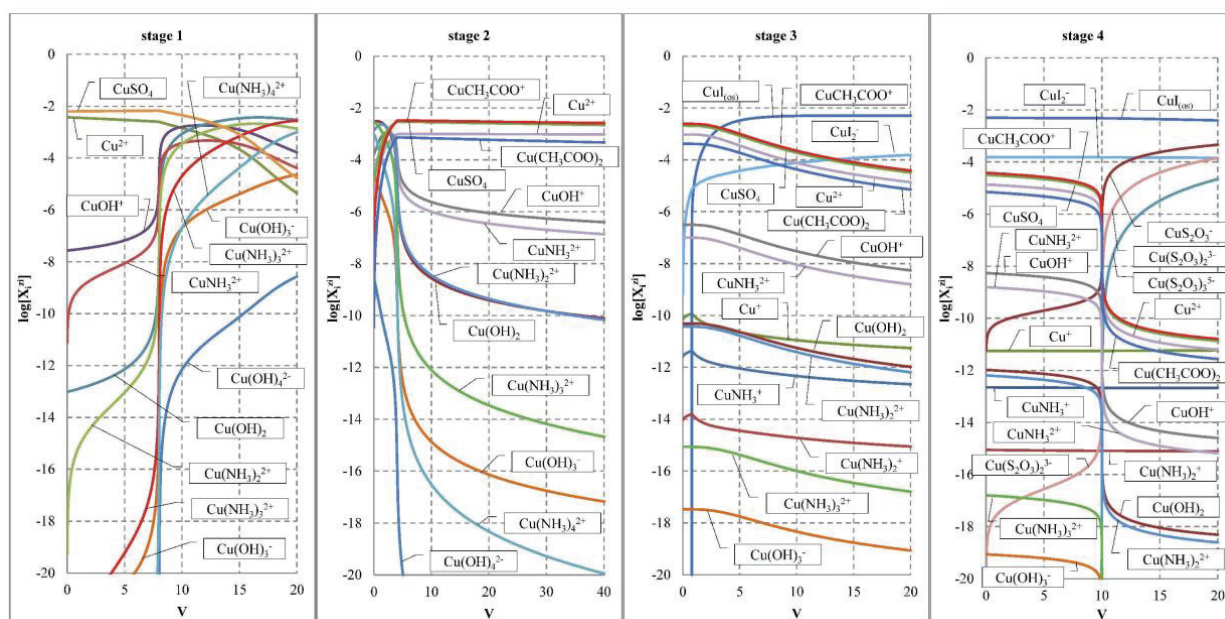
**Figure 9.** The speciation plots for indicated Cu-species within the successive stages. The $V$-values on the abscissas correspond to successive addition of V mL of: 0.25 mol/L $NH_3$ (stage 1); 0.75 mol/L $CH_3COOH$ (stage 2); 2.0 mol/L KI (stage 3); and 0.1 mol/L $Na_2S_2O_3$ (stage 4). For more details see text.
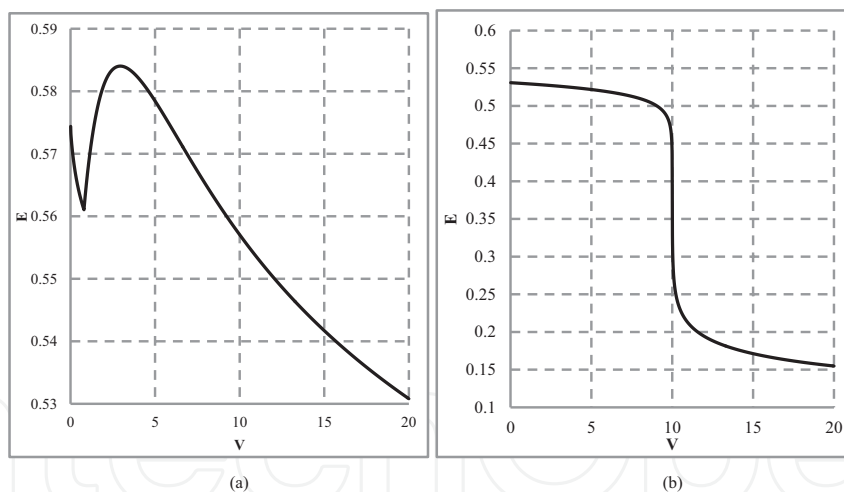


**Figure 10.** Plots of $E$ versus $V$ for (a) stage 3 and (b) stage 4.

addition of 0.795 mL of 2.0 mol/L KI (**Figure 11a**). Subsequently, the curve in **Figure 10**a increases, reaches a maximum and then decreases. At a due excess of the KI ($C_3$) added on the stage 3 ($V_K$ = 20 mL), solid iodine ($I_{2(s)}$, of solubility 0.00133 mol/L at 25°C) is not precipitated.
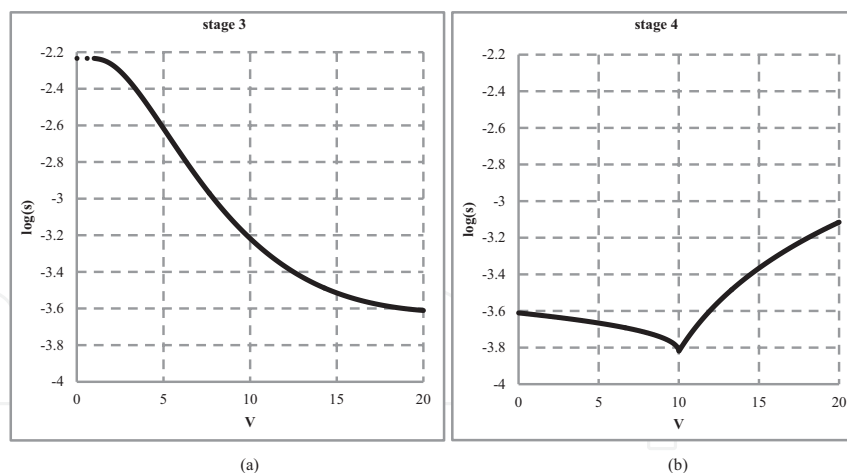
**Figure 11.** Solubility s of **CuI** within stage 3 (a) and stage 4 (b).

# 8. Final comments

The solubility and dissolution of sparingly soluble salts in aqueous media are among the main educational topics realized within general chemistry and analytical chemistry courses. The principles of solubility calculations were formulated at a time when knowledge of the two-phase electrolytic systems was still rudimentary. However, the earlier arrangements persisted in subsequent generations [81], and little has changed in the meantime [82]. About 20 years ago, Hawkes put in the title of his article [83] a dramatic question, corresponding to his statement presented therein that "the simple algorithms in introductory texts usually produce dramatic and often catastrophic errors"; it is hard not to agree with this opinion.

In the meantime, Meites et al. [84] stated that "It would be better to confine illustrations of the solubility product principle to 1:1 salts, like silver bromide (…), in which the (…) calculations will yield results close enough to the truth." The unwarranted simplifications cause confusion in teaching of chemistry. Students will trust us enough to believe that a calculation we have taught must be generally useful.

The theory of electrolytic systems, perceived as the main problem in the physicochemical studies for many decades, is now put on the side. It can be argued that the gaining of quantitative chemical knowledge in the education process is essentially based on the stoichiometry and proportions.

Overview of the literature indicates that the problems of dissolution and solubility calculation are not usually resolved in a proper manner; positive (and sole) exceptions are the studies and practice made by the authors of this chapter. Other authors, e.g., [13, 85], rely on the simplified schemes (ready-to-use formulas), which usually lead to erroneous results, expressed by dissolution denoted as $s^*$ [mol/L]; the values for $s^*$ are based on stoichiometric reaction notations and expressions for the solubility product values, specified by Eqs. (1) and (2). The calculation

of s* contradicts the common sense principle; this was clearly stated in the example with **Fe(OH)$_3$** precipitate. Equation (27) was applied to struvite [50] and dolomite [86], although these precipitates are nonequilibrium solid phases when introduced into pure water, as were proved in Refs. [20–23]. The fact of the struvite instability was known at the end of nineteenth century [49]; nevertheless, the formula s* = $(K_{sp})^{1/3}$ for struvite may be still encountered in almost all textbooks and learning materials; this problem was raised in Ref. [15]. In this chapter, we identified typical errors involved with s* calculations, and indicated the proper manner of resolution of the problem in question.

The calculations of solubility s*, based on stoichiometric notation and Eq. (3), contradict the calculations of s, based on the matter and charge preservation. In calculations of s, all the species formed by defined element are involved, not only the species from the related reaction notation. A simple zeroing method, based on charge balance equation, can be applied for the calculation of pH = pH$_0$ value, and then for calculation of concentrations for all species involved in expression for solubility value.

The solubility of a precipitate and the pH-interval where it exists as an equilibrium-solid phase in two-phase system can be accurately determined from calculations based on charge and concentration balances, and complete set of equilibrium constant values referred to the system in question.

In the calculations performed here we assumed *a priori* that the $K_{sp}$ values in the relevant tables were obtained in a manner worthy of the recognition, i.e., these values are true. However, one should be aware that the equilibrium constants collected in the relevant tables come from the period of time covering many decades; it results from an overview of dates of references contained in some textbooks [31, 85] relating to the equilibrium constants. In the early literature were generally presented the results obtained in the simplest manner, based on $K_{sp}$ calculation from the experimentally determined s* value, where all soluble species formed in solution by these ions were included on account of simple cations and anions forming the expression for $K_{sp}$. In many instances, the $K_{sp}$* values should be then perceived as conditional equilibrium constants [87]. Moreover, the differences between the equilibrium constants obtained under different physicochemical conditions in the solution tested were credited on account of activity coefficients, as an antidote to any discrepancies between theory and experiment.

First dissociation constants for acids were published in 1889. Most of the stability constants of metal complexes were determined after the announcement 1941 of Bjerrum's works, see Ref. [88], about ammine-complexes of metals, and research studies on metal complexes were carried out intermittently in the twentieth century [89]. The studies of complexes formed by simple ions started only from the 1940s; these studies were related both to mono- and two-phase systems. It should also be noted that the first mathematical models used for determination of equilibrium constants were adapted to the current computing capabilities. Critical comments in this regard can be found, among others, in the Beck [90] monograph; the variation between the values obtained by different authors for some equilibrium constants was startling, and reaching 20 orders of magnitude. It should be noted, however, that the determination of a set of stability constants of complexes as parameters of a set of suitable algebraic equations requires complex mathematical models, solvable only with use of an iterative computer program [91–93].

The difficulties associated with the resolution of electrolytic systems and two-phase systems, in particular, can be perceived today in the context of calculations using (1°) spreadsheets (2°) iterative calculation methods. In (1°), a calculation is made by the zeroing method applied to the function with one variable; both options are presented in this chapter.

The expression for solubility products, as well as the expression of other equilibrium constants, is formulated on the basis of mass action law (MAL). It should be noted, however, that the underlying mathematical formalism contained in MAL does not inspire trust, to put it mildly. For this purpose, the equilibrium law (EL) based on the Gibbs function [94] and the Lagrange multipliers method [95–97] with laws of charge and elements conservation was suggested lately by Michałowski.

From semantic viewpoint, the term "solubility product" is not adequate, e.g., in relation to Eq. (8). Moreover, $K_{sp}$ is not necessarily the product of ion concentrations, as indicated in formulas (4), (5), and (11). In some (numerous) instances of sparingly soluble species, e.g., sulfur, solid iodine, 8-hydroxyquinoline, dimethylglyoxime, the term solubility product is not applied. In some instances, e.g., for **$MnO_2$**, this term is doubtful.

One of the main purposes of the present chapter is to familiarize GEB within GATES as GATES/GEB to a wider community of analysts engaged in electrolytic systems, also in aspect of solubility problems.

In this context, owing to large advantages and versatile capabilities offered by GATES/GEB, it deserves a due attention and promotion. The GATES is perceived as a step toward reduction-ism [19, 71] of chemistry in the area of electrolytic systems and the GEB is considered as a general law of nature; it provides the real proof of the world harmony, harmony of nature.

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# References

[1]  Clever HL, Gevantman LH. Obituary: A.S. Kertes. Pure and Applied Chemistry. 1989;**61**: 121. http://dx.doi.org/10.1351/pac198961020121

[2]  Clever L, The IUPAC solubility data project. A brief history: 1972–2001. Chemistry International. 2004;**26**(3). http://www.iupac.org/publications/ci/2004/2603/4_clever.html

[3]  Gamsjäger H, Lorimer JW, Salomon M, Shaw DG, Tomkins RPT. The IUPAC-NIST solubility data series: A guide to preparation and use of compilations and evaluations (IUPAC Technical Report). Pure and Applied Chemistry. 2010;**82**(5):1137-1159. DOI: 10.1351/PAC-REP-09-10-33

[4]  Dirkse TP, Michałowski T, Akaiwa H, Izumi F. Copper, Silver, Gold and Zinc, Cadmium, Mercury Oxides and Hydroxides, Solubility Data Series. Vol. 23. Oxford: Pergamon; 1986. http://www.worldcat.org/title/copper-silver-gold-and-zinc-cadmium-mercury-oxides--and-hydroxides/oclc/12945958

[5]  Yalkowsky SH. Handbook of Aqueous Solubility Data (e-Book Google). CRC Press, LLC, Boca Raton, FL. 2003

[6]  Kobayashi T, Sasaki T, Takagi I, Moriyama H. Solubility of zirconium (IV) hydrous oxides. Journal of Nuclear Science and Technology. 2007;**44**(1):90-94. http://dx.doi.org/10.1080/18811248.2007.9711

[7]  Michałowski T, Lesiak A. Formulation of generalized equations for redox titration curves. Chemia Analityczna (Warsaw). 1994;**39**:623-637

[8]  Michałowski T. Application of GATES and MATLAB for resolution of equilibrium, metastable and non-equilibrium electrolytic systems. In: Michałowski T, editor. Applications of MATLAB in Science and Engineering. Rijeka: InTech-Open Access Publisher in the Fields of Science, Technology and Medicine; 2011. pp. 1-34. Chapter 1. http://www.intechopen.com/books/show/title/applications-of-matlab-in-science-and-engineering. ISBN 978-953-307-708-6

[9]  Michałowski T, Toporek M, Michałowska-Kaczmarczyk AM, Asuero AG. New trends in studies on electrolytic redox systems. Electrochimica Acta. 2013;**109**:519-531. DOI: http://dx.doi.org/10.1016/j.electacta.2013.07.125

[10]  Michałowska-Kaczmarczyk AM, Toporek M, Michałowski T. Speciation diagrams in dynamic iodide + dichromate system. Electrochimica Acta. 2015;**155**:217-227. DOI: http://dx.doi.org/10.1016/j.electacta.2015.01.003

[11]  Meija J, Michałowska-Kaczmarczyk AM, Michałowski T. Redox titration challenge. Analytical and Bioanalytical Chemistry. 2017;**409**(1):11-13. DOI 10.1007/s00216-016-0020-0

[12]  Michałowski T, Michałowska-Kaczmarczyk AM, Meija J, Solution of redox titration challenge, Analytical and Bioanalytical Chemistry, be issued in 409(17).

[13]  Kotrlý S, Šůcha L, Handbook of Chemical Equilibria in Analytical Chemistry, Ellis Horwood Limited, Halsted Press, a division of John Wiley & Sons, New York 1985.

[14]  Michałowski T. Calculations in Analytical Chemistry with Elements of Computer Programming (in Polish). Cracow: PK; 2001 http://suw.biblos.pk.edu.pl/resourceDetails&rId=3974

[15]  Michałowska-Kaczmarczyk AM, Asuero AG, Michałowski T. "Why not stoichiometry" versus "Stoichiometry—why not?" Part I. General context. Critical Reviews in Analytical Chemistry. 2015;**45**(2):166-188. DOI: 10.1080/10408347.2014.937852

[16] Michałowska-Kaczmarczyk AM, Michałowski T. Calculation of solubility of oxyquinolinates. Journal of Analytical Sciences, Methods and Instrumentation. 2014;**4**(3):71-79. DOI: 10.4236/jasmi.2014.43010

[17] Michałowska-Kaczmarczyk AM, Michałowski T. Solubility product challenge. Analytical and Bioanalytical Chemistry. 2015;**407**(6):1789-1791

[18] Michałowska-Kaczmarczyk AM, Michałowski T. Solution to the solubility product challenge. Analytical and Bioanalytical Chemistry. 2015;**407**(17):4877-4878

[19] Michałowski T. Constructivist perception of chemical knowledge. Implications in terms of electrolytic systems (in Polish). In: Use of Information Technology in Academic Teaching of Chemistry (Maciejowska I, Ruszak M, Witkowski S, eds.), Jagiellonian University, Cracow, 2007. pp. 130–136. http://www2.chemia.uj.edu.pl/~ictchem/book.html

[20] Michałowski T, Pietrzyk A. A thermodynamic study of struvite+water system. Talanta. 2006;**68**:594-601

[21] Michałowski T, Pietrzyk A. Quasistatic processes in non-equilibrium two-phase systems with ternary salts: I. Struvite + aqueous solution ($CO_2$ + KOH). Chemia Analityczna (Warsaw). 2008;**53**:33-46

[22] Michałowski T, Borzęcka M, Toporek M, Wybraniec S, Maciukiewicz P, Pietrzyk A. Quasistatic processes in non-equilibrium two-phase systems with ternary salts: II. Dolomite + aqueous media. Chemia Analityczna (Warsaw). 2009;**54**:1203-1217

[23] Michałowski T, Asuero AG, Thermodynamic modelling of dolomite behavior in aqueous media. Journal of Thermodynamics. 2012;(2012):12. Article ID 723052. DOI: 10.1155/2012/723052. http://www.hindawi.com/journals/jtd/2012/723052/cta/

[24] http://www.thefreedictionary.com/ternary

[25] Bartecki A. On the chemistry of $MeO_2^{n+}$ oxycation compounds. Chemické Zvesti. 1965;**19**:161-166

[26] Pauling L. The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry. 3rd ed. Ithaca, New York: Cornell University Press; 1960

[27] López FA, Alguacil FJ, Roman CP, Tayibi H, López-Delgado A. Disposal of elemental mercury via sulphur reaction by milling; 1 st International Conference on "Hazardous Waste Management", 1–3 Octubre, Chaina, Grete, Greece 2008, p. 49. http://digital.csic.es/bitstream/10261/7692/1/DISPOSAL%20ELEMENTALHg.pdf

[28] Chadwick BM, Sharpe AG. Transition metal cyanides and their complexes. In: Emeleus HJ, Sharpe AG, editors. Advances in Inorganic Chemistry and Radiochemistry. Vol. 8. New York: Academy Press Inc.; 1966. p. 118

[29] Michałowski T, Nizińska-Pstrusińska M, Sztark W, Baterowicz A. Laboratory Trainings in Analytical Chemistry (in Polish). Kraków: Wyd. PK; 2002. http://bc.biblos.pk.edu.pl/

bc/resources/MD/MichalowskiT/CwiczeniaLaboratoryjne/pdf/MichalowskiT_Cwicze-niaLaboratoryjne.pdf

[30]  http://en.wikipedia.org/wiki/Solubility_equilibrium

[31]  Inczédy J, Analytical applications of complex equilibria, Chichester, E. Horwood, New York, Halsted Press, 1976.

[32]  Ruetschi P, Giovanoli R. The behaviour of $MnO_2$ in strongly acidic solutions. Journal of Applied Electrochemistry. 1982;**12**(1):109-114. DOI: 10.1007/BF01112071

[33]  Nikolsky BP, editors. Chemist's Handbook (in Russian). Vol. III. Moscow: Khimia; 1964

[34]  Michałowska-Kaczmarczyk AM, Rymanowski M, Asuero AG, Toporek M, Michałowski T. Formulation of titration curves for some redox systems. American Journal of Analytical Chemistry.  2014;**5**:861-878.  http://www.scirp.org/journal/PaperInformation.aspx?paperID= 50016#.VGOZ92dvHFw.

[35]  https://answers.yahoo.com/question/index?qid=20070415234848AA54Gus

[36]  Hulanicki, A., Reactions of acids and bases in analytical chemistry, Chichester, West Sussex, England : E. Horwood ; New York : Halsted Press ; Warsaw : PWN-Polish Scientific Publishers, 1987. https://iucat.iu.edu/iun/3772927

[37]  Gordus AA. Chemical equilibrium, VIII. Precipitates. Journal of Chemical Education. 1991;**68**(11):927-930. http://dx.doi.org/10.1021/ed068p927.

[38]  https://answers.yahoo.com/question/index?qid=20090316151751AAyF87o

[39]  https://en.wikipedia.org/wiki/Carbon_dioxide

[40]  Lurie YY. Handbook of Analytical Chemistry (in Russian). Moscow: Izd. Khimia; 1971. s. 105

[41]  deCogan D. Transmission Line Matrix (TLM) Techniques for Diffusion Applications. Australia: Gordon and Breach Science Publishers; 1998. p. 134

[42]  Considine DM, Considine GD. Van Nostrand's Scientific Encyclopedia. 8th ed. New York: Springer Science+Business Media, LLC; 1995. p. 673

[43]  https://answers.yahoo.com/question/index?qid=20080518113447AAg17u3

[44]  Michałowski T. Evaluation of the systematic error related to determination of chloride according to Mohr method. Chemia Analityczna (Warsaw). 1989;**34**:461

[45]  Meija J, Michałowska-Kaczmarczyk AM, Michałowski T. Mohr's method Challenge. Analytical and Bioanalytical Chemistry. 2016;**408**(7):1721-1722. http://paperity.org/p/ 75256979/mohrs-method-challenge

[46]  Meija J, Michałowska-Kaczmarczyk AM, Michałowski T. Solution to Mohr's method challenge. Analytical and Bioanalytical Chemistry. 2016;**408**(17):4469-4471. DOI: 10.1007/ s00216-015-9273-2

[47] E.P. Leite (Ed.), Matlab - Modelling, Programming and Simulations, Sciyo, Published by Sciyo, Rijeka, Croatia 2010. ISBN 978-953-307-125-1. http://www.intechopen.com/books/matlab-modelling-programming-and-simulations

[48] Michałowska-Kaczmarczyk AM, Michałowski T. Evaluation of transition points between different solid phases in aqueous media. Journal of Analytical Sciences, Methods and Instrumentation. 2014;**4**(3):87-94. http://www.scirp.org/journal/PaperInformation.aspx?PaperID=49567#.VGOZo2dvHFw

[49] Beilstein F, Grosset Th. Ueber die Bestimmung der freien Schwefelsaure in der Schwefelsauren Thonerde. Zeitschrift für Analytische Chemie. 1890;**29**:73-78

[50] Doyle JD, Parsons SA. Struvite formation, control and recovery. Water Research. 2002;**36**(16):3925-3940

[51] http://chemlab.truman.edu/CHEM222manual/pdf/nickelgrav.pdf

[52] Michałowski T. Calculation of pH and potential E for bromine aqueous solution. Journal of Chemical Education. 1994;**71**:560-562. DOI: 10.1021/ed071p560

[53] Michałowski T, Lesiak A. Acid-base titration curves in disproportionating redox systems. Journal of Chemical Education. 1994;**71**:632-636. DOI: 10.1021/ed071p632

[54] Michałowski T, Wajda N, Janecki D. A unified quantitative approach to electrolytic systems. Chemia Analityczna (Warsaw). 1996;**41**:667-685. http://www.chem.uw.edu.pl/chemanal/PDFs/1996/CHAN1996V0041P00667.pdf

[55] Michałowski T, Baterowicz A, Madej A, Kochana J. An extended Gran method and its applicability for simultaneous determination of Fe(II) and Fe(III). Analytica Chimica Acta. 2001;**442**(2):287-293. http://www.sciencedirect.com/science/article/pii/S0003267001011722

[56] Michałowski T, Toporek M, Rymanowski M. Overview on the Gran and other linearization methods applied in titrimetric analyses. Talanta. 2005;**65**(5):1241-1253. http://pl.scribd.com/doc/173699711/Talanta-65-2005-1241-1253

[57] Michałowski T, Rymanowski M, Pietrzyk A. Non-typical Brönsted's acids and bases. Journal of Chemical Education. 2005;**82**(3):470-472. http://pubs.acs.org/doi/abs/10.1021/ed082p470

[58] Michałowski T, Kupiec K, Rymanowski M. Numerical analysis of the Gran methods. A comparative study. Analytica Chimica Acta. 2008;**606**(2):172-183. http://www.sciencedirect.com/science/article/pii/S0003267007018673

[59] Ponikvar M, Michałowski T, Kupiec K, Wybraniec S, Rymanowski M. Experimental verification of the modified Gran methods applicable to redox systems. Analytica Chimica Acta. 2008;**628**(2):181-189. http://pl.scribd.com/doc/173699262/ACA-2008-2

[60] Michałowski T, Pietrzyk A. The generalized electron balance concept. Derivation based on elementary rules of the matter conservation. In: Zuba D, Parczewski A, editors.

Chemometrics: Methods and Applications. Institute of Forensic Research, Kraków; 2006. pp. 415-422. https://pbn.nauka.gov.pl/sedno-webapp/works/210292

[61] Michałowski T. Electron Balance as the Basis of Calculations in Redox Systems (in Polish). In: Use of Information Technology in Academic Teaching of Chemistry (Maciejowska I, Ruszak M, Witkowski S, eds.), Jagiellonian University, Cracow, 2007. pp. 162-169. http://www.chemia.uj.edu.pl/~ictchem/book.html

[62] Michałowski T, Pietrzyk A. Complementarity of physical and chemical laws of preservation in aspect of electrolytic systems (in Polish). Wiadomości Chemiczne. 2007;**61**:625-640

[63] Michałowska-Kaczmarczyk AM, Asuero AG, Toporek M, Michałowski T. "Why not stoichiometry" versus "Stoichiometry – why not?" Part II. GATES in context with redox systems. Critical Reviews in Analytical Chemistry. 2015;**45**(3):240-268. http://www.tandfonline.com/doi/full/10.1080/10408347.2014.937853

[64] Michałowska-Kaczmarczyk AM, Michałowski T, Toporek M, Asuero AG. "Why not stoichiometry" versus "Stoichiometry – why not?" Part III. Extension of GATES/GEB on Complex Dynamic Redox Systems. Critical Reviews in Analytical Chemistry. 2015;**45**(4):348-366. DOI: 10.1080/10408347.2014.953673. http://www.researchgate.net/publication/274401037_Why_Not_Stoichiometry_Versus_Stoichiometry_-_Why_Not_Part_III_Extension_of_GatesGeb_on_Complex_Dynamic_Redox_Systems

[65] Michałowska-Kaczmarczyk AM, Michałowski T, Toporek M. Formulation of dynamic redox systems according to GATES/GEB principles. International Journal of Electrochemical Science. 2016;**11**:2560-2578. DOI:10.20964/e110340

[66] Michałowski T, Ponikvar-Svet M, Asuero AG, Kupiec K. Thermodynamic and kinetic effects involved with pH titration of As(III) with iodine in a buffered malonate system. Journal of Solution Chemistry. 2012;**41**(3):436-446. http://www.springerlink.com/content/p2m73068h2q5u174/. DOI: 10.1007/s10953-012-9815-6

[67] Michałowska-Kaczmarczyk AM, Michałowski T. Comparative balancing of non-redox and redox electrolytic systems and its consequences. American Journal of Analytical Chemistry. 2013;**4**(10):46-53. http://www.scirp.org/journal/PaperInformation.aspx?PaperID=38569

[68] Toporek M, Michałowska-Kaczmarczyk AM, Michałowski T. Disproportionation reactions of HIO and NaIO in static and dynamic systems. American Journal of Analytical Chemistry. 2014;**5**:1046-1056. http://www.scirp.org/journal/PaperInformation.aspx?PaperID=51637#.VHXKcWfpt74

[69] Michałowska-Kaczmarczyk AM, Michałowski T. Generalized electron balance for dynamic redox systems in mixed-solvent media. Journal of Analytical Sciences, Methods and Instrumentation. 2014;**4**(4):102-109. http://www.scirp.org/Journal/PaperInformation.aspx?PaperID=52018#.VH1N5Gfpt74

[70] Michałowska-Kaczmarczyk AM, Michałowski T. Compact formulation of redox systems according to GATES/GEB principles. Journal of Analytical Sciences, Methods and Instrumentation. 2014;**4**(2):39-45. http://www.scirp.org/journal/PaperInformation.aspx?PaperID=46335

[71] Michałowska-Kaczmarczyk AM, Michałowski T. GATES as the unique tool for simulation of electrolytic redox and non-redox systems. Journal of Analytical & Bioanalytical Techniques. http://omicsonline.org/open-access/gates-as-the-unique-tool-for-simulation-of-electrolytic-redox-and-non-redox-systems-2155-9872.1000204.pdf

[72] Michałowski T, Pilarski B, Asuero AG, Michałowska-Kaczmarczyk AM. Modelling of acid-base properties in binary-solvent systems. In: Wypych G, editor. Handbook of Solvents, Vol. 1. Properties. Toronto: ChemTec Publishing; 2014. pp. 623-648. Chapter 9.4

[73] Michałowski T, Michałowska-Kaczmarczyk AM, Toporek M. Formulation of general criterion distinguishing between non-redox and redox systems. Electrochimica Acta. 2013;**112**:199-211. http://www.sciencedirect.com/science/article/pii/S0013468613016836

[74] Toporek M, Michałowska-Kaczmarczyk AM, Michałowski T. Symproportionation versus disproportionation in bromine redox systems. Electrochimica Acta. 2015;**171**:176-187. http://www.sciencedirect.com/science/article/pii/S0013468615011238

[75] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T. A Distinguishing Feature of the Balance $2 \cdot f(O) - f(H)$ in Electrolytic Systems. The Reference to Titrimetric Methods of Analysis, in: "Titration", InTech 2017

[76] Michałowska-Kaczmarczyk AM, Spórna-Kucab A, Michałowski T. Principles of Titrimetric Analyses According to Generalized Approach to Electrolytic systems (GATES), in: "Titration", InTech 2017

[77] AM, Spórna-Kucab A, Michałowski T. Generalized Electron Balance (GEB) as the Law of Nature in Electrolytic Redox Systems, in: "Redox: Principles and Advanced Applications", InTech 2017.

[78] Pietrzyk A, Michałowski T. Computer simulation of the process of struvite $MgNH_4PO_4 \cdot 6H_2O$ dissolution in aqueous solutions, (in Polish). Use of Information Technology in Academic Teaching of Chemistry. Kraków: UJ; 2007. pp.137-146. http://www.chemia.uj.edu.pl/~ictchem/book.html

[79] Pietrzyk A, Michałowski T, Conditions of struvite formation in aqueous systems. In: Zuba D, Parczewski A, editors. Chemometrics: Methods and Applications. Kraków; 2006. pp. 423-427. https://pbn.nauka.gov.pl/works/210292

[80] Steudel R, editor. Elemental Sulfur and Sulfur-Rich Compounds. II. Topics in Current Chemistry. Berlin, Heidelberg: Springer-Verlag; 2003

[81] Clark RW, Bonicamp JM. The $K_{sp}$-solubility conundrum. Journal of Chemical Education. 1998;**75**(9):1182-1185. DOI: 10.1021/ed075p1182

[82] Umland JB, Bellama JM. General Chemistry. 2nd ed. Minneapolis, MN: West; 1996. pp. 621-622

[83] Hawkes SJ. What should we teach beginners about solubility and solubility products? Journal of Chemical Education. 1998;**75**(9):1179-1181. DOI: 10.1021/ed075p1179

[84] Meites L, Pode JSF, Thomas HC. Are solubilities and solubility products related? Journal of Chemical Education. 1966;**43**:667-672

[85] Šůcha L, Kotrlý S. Solution Equilibrium in Analytical Chemistry. London: Van Nostrand Reinhold Comp.; 1975

[86] Chen G, Tao D. Effect of solution chemistry on flotability of magnesite and dolomite. International Journal of Mineral Processing. 2004;**74**(1–4):343-357

[87] Ringbom A. Complexation in Analytical Chemistry. New York: Interscience Publishers; 1963

[88] Rossotti H. The study of ionic equilibria. An introduction. London: Longman; 1978

[89] Sillén LG, Martell AE, Stability Constants of Metal-Ion Complexes, The Chemical Society, London, 1964; Supplement No. 1, 1971.

[90] Beck MT. Chemistry of Complex Equilibria. New York: Van Nostrand Reinhold Co.; 1970

[91] Janecki D, Doktór K, Michałowski T. Determination of stability constants of complexes of $M_iK_jH_kL$ type in concentrated solutions of mixed salts. Talanta. 1999;**48**:1191-1197 http://www.sciencedirect.com/science/article/pii/S0039914098003452

[92] Janecki D, Doktór K, Michałowski T. Erratum to "Determination of stability constants of complexes of $M_jK_jH_kL$ type in concentrated solutions of mixed salts" [48 (1999) 1191]. Talanta. 1999;**49**:943. http://www.sciencedirect.com/science/article/pii/S0039914099001745

[93] Janecki D, Styszko-Grochowiak K, Michałowski T. The catenation and isomerisation effects on stability constants of complexes formed by some diprotic acids. Talanta. 2000;**52**:555-562. http://www.ncbi.nlm.nih.gov/pubmed/18968016

[94] https://en.wikipedia.org/wiki/Gibbs_free_energy

[95] Zeidler E. Nonlinear Functional Analysis and its Applications: III: Variational Methods and Optimization. New York: Springer Science +Business Media; 1985

[96] Sieniutycz S. Thermodynamic Approaches in Engineering Systems. Amsterdam: Elsevier; 2016

[97] Bertsekas DP. Nonlinear Programming. 2nd ed. Cambridge, MA: Athena Scientific; 1999