MODELING OF PHYSICO-CHEMICAL PROCESSES BASED ON MASS BALANCE AND GENERALIZED EQUATIONS FOR MULTICOMPONENT TWO-PHASE AQUATIC ECOSYSTEMS

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Abstract

The paper presents a model of physico-chemical processes in aquatic ecosystems, utilizing mass balance equations for multicomponent two-phase systems. This model aims to provide a comprehensive understanding of the interactions and dynamics within aquatic environments. It presents original mass balance equations within the residual concentration method to analyze thermodynamic functions for various natural chemical equilibria, described by the developed generalized equations. By incorporating mass balance equations, the study addresses the distribution and transformation of various chemical species between natural waters and sediment phases. The approach allows for the simulation of complex processes such as adsorption, desorption, and chemical reactions in a detailed and systematic manner. The method demonstrates the ability to handle simultaneous formation of multiple chemical species and derive specific thermodynamic relationships. It provides a comprehensive analysis of thermodynamic conditions, estimating solid phase quantities based on initial composition and pH values. Applied to several real systems, the approach shows strong agreement with experimental findings, validating its robustness and applicability. The developed model can be used to predict the behavior of pollutants, nutrients, and other substances in aquatic ecosystems, offering valuable insights for environmental management and conservation efforts.

Keywords: *complexing agent, global thermodynamic functions, heterogeneous multicomponent system, mass balance conditions, saturated solution*

1. INTRODUCTION

Aquatic ecosystems are complex environments where numerous physico-chemical processes occur simultaneously, influencing the distribution and fate of various chemical species. Understanding these processes is crucial for effective environmental management and conservation. This study is focused on modeling of these processes based on mass balance equations for multicomponent two-phase systems, providing a detailed framework for analyzing the interactions and dynamics within aquatic environments.

The model incorporates fundamental mass balance equations within the residual concentration (**RC**) method for heterogeneous systems, specifically focusing on the two-phase systems "*solid phase - saturated multicomponent solution*", to account for the distribution and transformation of chemical species between the water and sediment phases. By simulating complex natural processes such as adsorption, desorption, and chemical reactions, the model offers a comprehensive understanding of the behavior of pollutants, nutrients, and other substances in aquatic ecosystems. This approach not only enhances our knowledge of these environments but also aids in predicting the impact of various environmental changes and anthropogenic activities. The development and application of this model are essential for advancing our ability to manage and protect aquatic ecosystems. By providing

valuable insights into the physico-chemical processes that govern these systems, the study contributes to more informed decision-making in environmental management and policy.

The study of heterogeneous systems using the *RC* method is often accompanied by variations in parameters used to construct "*property-composition*" diagrams, such as electromotive force, light adsorption, apparent volume of precipitates, electrical conductivity, refractive index, density, and pH of solutions. Within the *RC* method, the concentrations of compounds in the solution volume must also be known. For the study, one of two series of mixtures is prepared: a series of mixtures with a constant concentration of the metal ion and variable concentration of the ligand, or a series with a constant total concentration of the metal ion and the ligand. After the heterogeneous mixture reaches equilibrium, the solid phase is separated from the liquid phase, the pH of the solution is measured, and the residual concentrations of various ions are determined. Subsequently, the content of each ion in the precipitate Δm_i is calculated as the difference between the amount of ion in the mixture m_i^0 and the amount of ion in the solution m_i^r :

$$\Delta m_i = m_i^0 - m_i^r ,$$

or recalculating for the volume of the mixture (in terms of concentrations):

$$\Delta C_i = C_i^0 - C_i^r ,$$

where ΔC_i is the amount of ion in the solid phase, expressed in mol/L.

This paper investigates thermodynamic functions for various chemical interactions in aqueous ecosystems, described by the developed generalized equation, including metal ion hydrolysis, ligand protonation, and complex formation, described by the introduced generalized reaction equation. The research examines a variety of solid phases characterized by a general formula involving metal ions, hydroxides, anions, and ligands. The solubility of these solid phases is determined by heterogeneous equilibrium.

The derivation of the mass balance (**MB**) equation for the metal ion involves accounting for the contributions from the solid phase, which represents the amount of precipitated metal ion per unit volume of the solution. This is combined with the inputs from hydroxocomplexes, complexes with inorganic and organic complexing agents, and others, typically under conditions where ligands are in excess. The equation expresses the total (initial) concentration of the metal ion in the heterogeneous mixture and its residual concentration in the aqueous solution.

From the stoichiometric composition of the solid phases, in this work specific thermodynamic relationships are derived, involving the changes in concentration of the metal ion, anions, ligands, and hydroxides. When the anion is precipitated, the mass balance equation also considers its potential protonation and the formation of neutral and mixed complexes with the metal ion. This method demonstrates the ability to account for the simultaneous formation of two insoluble species containing two metal ions or anions.

Our innovative approach involves a thorough analysis of the thermodynamic conditions that govern various processes by examining overarching thermodynamic characteristics [1-4]. Utilizing a complete set of thermodynamic functions allows estimation of solid phase quantities based on initial heterogeneous mixture composition and solution pH values. The proposed thermodynamic approach can be extended to more complex systems that involve additional reactions and complex formations.

Applying the developed approach, several real systems have been investigated. By employing an advanced thermodynamic model to simulate precipitation alongside key parameters, such as initial concentrations in both the liquid and solid phases, the study achieves a strong agreement with experimental findings for various real systems.

At the beginning, the thermodynamics of heterogeneous processes of precipitation-dissolution of slightly soluble salts of different nature and arbitrary composition are examined under conditions where various secondary reactions occur between the ions of the solid phase and the components of the saturated aqueous solution. Secondary reactions include protonation of the ligand, hydrolysis of the

metal ion, and formation of neutral complexes, protonated complexes, and hydroxocomplexes. To this end, an original method is used to study complex chemical equilibria in the presence of solid phases. First of all, the notion of a generalized reaction equation is introduced to account for all associated secondary reactions. This equation represents the generalization of a set of usual chemical equations, considering the simultaneous formation of several different soluble chemical species. The necessity to examine an integral (general) process arises from the fact that the nature and concentration ratios of the compounds (complex species) produced in the reactions depend on the ratio of the reactants (metal ion and ligand), temperature, and other factors (thermodynamic parameters).

Based on the generalized mass balance equations for multicomponent two-phase systems, thermodynamic functions can be calculated under real-world conditions. This thermodynamic analysis of equilibrium conditions enables the examination of various chemical interactions in aqueous ecosystems, such as the hydrolysis of metal ions, protonation of ligands, and complex formation, from a unified perspective. Special attention is given to the influence of pH on the variations of thermodynamic functions, considering the significant role of hydrogen ions in many chemical reactions in aqueous solutions. The approach outlined in this paper progresses from simple to complex analyses, ultimately addressing even more intricate systems, providing a comprehensive framework for understanding physico-chemical processes in aquatic ecosystems.

2. THEORETICAL PART

2.1. Generalized equation and the variation of the Gibbs energy for the general/integral process

From the variety of possible chemical transformations in solution involving the cation *M* and the anion *A* of a slightly soluble salt with a simple composition $MA_{(S)}$ (where the symbol "*S*" denotes the solid phase), the initial focus is on the hydrolysis of the cation and the protonation of the anion according to scheme *A*:

$$MA_{(S)} = M + A, \qquad K_S^0,\ \Delta H_S^0\ , \tag{1}$$

$$M + iH_2O = M(OH)_i + iH, \qquad K_i^0,\ \Delta H_i^0 \tag{2}$$

$$A\ + jH = H_jA, \qquad K_j^0,\ \Delta H_j^0 \tag{3}$$

Here, K_S^0, K_i^0 and K_j^0 represent the thermodynamic equilibrium constants and H_S^0, H_i^0 and H_j^0 are the standard enthalpy changes (here and henceforth, the charges of the species are omitted for convenience):

$$K_S^0 = a_M a_A \tag{4}$$

$$K_i^0 = \frac{a_{M(OH)_i} a_H^i}{a_M} \tag{5}$$

$$K_j^0 = \frac{a_{H_jA}}{a_A a_H^j} \tag{6}$$

Subsequently, indices *s*, *i*, and *j* denote all quantities related to the species $MA_{(S)}$, $M(OH)_i$ and H_jA or to the reactions (1)-(3). The variations of other thermodynamic functions, particularly ΔG and ΔS, are calculated using well-known thermodynamic relations:

$$\Delta G_S^0 = -RTln\ K_S^0 = \Delta H_S^0 - T\Delta S_S^0 \tag{7}$$

$$\Delta G_i^0 = -RTln\ K_i^0 = \Delta H_i^0 - T\Delta S_i^0 \tag{8}$$

$$\Delta G_j^0 = -RTln\ K_j^0 = \Delta H_j^0 - T\Delta S_j^0 \tag{9}$$

The subscript "*0*" for the equilibrium constants (4)-(6) indicates that these constants are thermodynamic. Concentration constants, correlated with the thermodynamic ones, will be used and defined by the relations:

$$K_S^0 = K_s \gamma_M \gamma_A \tag{10}$$

$$K_i^0 = K_i \frac{\gamma_i \gamma_H^i}{\gamma_M} \tag{11}$$

$$K_j^0 = K_j \frac{\gamma_j}{\gamma_A \gamma_H^j} \tag{12}$$

where γ denotes the activity coefficient of the respective species.

Further, the following task is formulated: *to calculate the variations of the thermodynamic functions of the integral process (1)-(3) under conditions different from standard ones*. To address this, the objective is to describe the integral process (1)-(3) with a single equation. Under the conditions where the metal ion is represented by a single hydroxocomplex $M(OH)_i$, and the anion exists in the form of a single protonated species H_jA, the equation of the integral heterogeneous process represents a simple combination of equations (1)-(3):

$$MA_{(S)} + (j\text{-}i)\, H + iH_2O = M(OH)_i + H_jA \tag{13}$$

In this case, the task is reduced to calculating the thermodynamic characteristics of the integral reaction (13). The thermodynamic relationships of this process are governed by the principles of classical thermodynamics. In particular, the variation of the thermodynamic functions of the integral reaction (13) is expressed linearly through the thermodynamic characteristics of reactions (1)-(3). Under real conditions, the metal ion and the anion are usually present in the saturated solution in the form of several hydroxocomplexes $M(OH)_i$ and protonated species H_jA. Therefore, it is necessary to generalize equation (13). For this purpose, to correctly account for the *MB*, it is assumed that the hydroxocomplexes and protonated species are formed as a result of the reaction in proportion to their partial molar fractions. These fractions are formulated as follows:

$$f_i = \frac{[\,M(OH)_i]}{C_M} = \frac{[\,M(OH)_i]}{\sum_{i=0}^{m}[\,M(OH)_i]} \tag{14}$$

$$f_j = \frac{[H_jA\,]}{C_A} = \frac{[H_jA\,]}{\sum_{j=0}^{n}[H_jA\,]} \tag{15}$$

Thus, the mass balance for the metal ion and anion is automatically considered correct, as $\sum_{i=0}^{m} f_i = 1$ and $\sum_{j=0}^{n} f_j = 1$. Subsequently, the respective amount of hydrogen ions and water molecules is added through a simple calculation. As a result, the generalized equation of the reactions takes the form:

$$MA_{(S)} + \left(\sum_{j=1}^{n} jf_j - \sum_{i=1}^{m} if_i\right)H + \left(\sum_{i=1}^{m} if_i\right)H_2O = \sum_{i=0}^{m} f_i\, M(OH)_i + \sum_{j=0}^{n} f_j\, H_jA \tag{16}$$

The specificity of this equation lies in the fact that the stoichiometric coefficients are variable quantities depending on the chemical composition of the system. For integer values of the partial molar fractions f_i and f_j, equation (16) takes the form of the trivial equation (13). Describing the equilibria in the "slightly soluble salt precipitate – aqueous solution" heterogeneous system using the generalized interaction equation has several advantages. Firstly, such an approach allows for the explicit determination of both the contribution of certain chemical species to the equilibrium process and the contribution of specific chemical equations that describe the complex chemical equilibrium. In other words, it reveals the stoichiometric aspects of chemical interactions in the system. Secondly, the thermodynamic analysis of the generalized equation (16) allows for the determination of any thermodynamic functions of the system. For example, the authors [1-3] have proven that the following thermodynamic expressions are valid for the generalized heterogeneous process (16):

$$\Delta G_S = -RTlnK_S\alpha_M\alpha_A + RTlnC_M^0 C_A^0 \tag{17}$$

$$\Delta H_S = \Delta H_S^0 + \sum_{i=1}^{m} f_i\, \Delta H_i^0 + \sum_{j=0}^{n} f_j \Delta H_j^0 \tag{18}$$

In equation (17) by C_M and C_A are denoted the total (analytical) concentrations of the metal ion and the anion in the mixture and

$$\propto_M = 1 + \sum_{i=1}^{m} K_i [H]^{-i} \quad (19)$$

$$\propto_A = 1 + \sum_{j=1}^{n} K_j [H]^{j} \quad (20)$$

From equation (18), it follows that among all thermodynamic functions, only the enthalpy change shows a sum of the individual reactions (1)-(3), and the contributions of reactions (2) and (3) are proportional to the partial molar fractions of the respective species $M(OH)_i$ and H_jA. Obviously, under standard conditions, this finding holds true only for the Gibbs energy change and does not apply to other functions. Therefore, the contribution of reactions (2) and (3) to the Gibbs energy variation of process (1) is expressed through the concentration coefficients $\propto_M$ and $\propto_A$. In the specialized literature, these concentration functions are well-known and referred to as secondary reaction coefficients. It is noteworthy that these functions involve not thermodynamic constants, but rather concentration coefficients.

Based on the sign and value of ΔG_S, the conditions for precipitation and the completeness of solid phase formation can be determined. If $\Delta G_S > 0$, then the equilibrium is shifted in the direction of precipitate formation. Conversely, if $\Delta G_S < 0$, its dissolution occurs. The equality $\Delta G_S = 0$ characterizes the condition for the onset of precipitation (dissolution) of the slightly soluble salt.

Equation (17) can be viewed as the sum of three components:

$$\Delta G_S = \Delta G(1) + \Delta G(2) + \Delta G(3),$$

where

$$\Delta G(1) = -RTlnK_S$$

$$\Delta G(2) = -RTln\alpha_M + RTlnC_M$$

$$\Delta G(3) = -RTln\alpha_A + RTlnC_A$$

Similarly, the generalized equation (16) can also be decomposed into three simpler equations:

$$MA_{(S)} = M + A$$

$$M + \left(\sum_{i=1}^{m} if_i\right) H_2O = \sum_{i=0}^{m} f_i\, M(OH)_i + \left(\sum_{i=1}^{m} if_i\right) H$$

$$A + \left(\sum_{j=1}^{n} jf_j\right) H = \sum_{j=0}^{n} f_j\, H_jA$$

An analogous analysis for the previous system "*slightly soluble salt - saturated aqueous solution*" in the presence of a ligand/chelating agent L, capable of forming complexes with the metal ion, shows that the Gibbs energy variation of the integral process is calculated using the same equation (17) with the difference that the calculation of the concentration function α_M becomes more complicated [4]. It should be noted that equation (17) remains valid even in the presence of polynuclear hydroxocomplexes; however, in this system, the coefficient α_M is determined by the expression:

$$\propto_M = 1 + \sum_i \sum_j iK_{M_i(OH)_j} [M]^{i-1} [H]^{-i} \quad (21)$$

It is important to note that in this scenario, determining the equilibrium concentration of the metal ion $[M]$ requires solving the mass balance equation:

$$C_M = \sum_{i=0} \sum_{j=1} i[M_i(OH)_j] = [M] \propto_M \quad (22)$$

In general, for the precipitate of a salt with composition $M_pA_{q(S)}$, analogous reasoning leads to the expression [5-7]:

$$\Delta G_S = -RTlnK_S \propto_M^p \propto_A^q + RTln(C_M^0)^p (C_A^0)^q \quad (23)$$

The thermodynamic approach to describing chemical equilibria in the system "*precipitate of a slightly soluble salt - aqueous solution*", described in this paper and developed in [8], allows for the introduction and calculation of the dependence of any thermodynamic functions of the system on experimental conditions (pH, total concentrations of reactants, etc.). This approach can be generalized in the case of the formation in solution of species with arbitrary compositions $M_i(OH)_pH_qL_j$ or $M_i(OH)_pH_qA_j$. However, the formation of polynuclear complex compounds leads to some peculiarities in the system behaviour [9-11].

In the "*slightly soluble hydroxide – solution*" system, the generalized interaction equation has the form:

$$M(OH)_{m(S)} = \sum_{i=0}^{m} f_{M(OH)_i} M(OH)_i + (n - \bar{m})OH \quad (24)$$

Here, $\bar{m}$ represents the Bjerrum function:

$$\bar{m} = \sum_{i=1}^{m} i f_{M(OH)_i} = \frac{\sum_{i=1}^{m} iK_i[H]^{-i}}{1+\sum_{i=1}^{m} K_i[H]^{-i}} \quad (25)$$

For the generalized process (24) the following thermodynamic expression is obtained:

$$\Delta G_S = -RTlnK_S \propto_M + RTlnC_M[H]^{-n} \quad (26)$$

The thermodynamic functions of the formation-dissolution reactions of the oxide precipitate with composition $M_nO_{m(S)}$ are described by similar expressions, except that the equilibrium constant K_S refers to the reaction:

$$\frac{1}{n}M_nO_{m(S)} + \frac{2m}{n}H = M + \frac{m}{n}H_2O, \quad K_S \quad (27)$$

The Gibbs energy variation of this reaction, taking into account the secondary reactions of the metal ion, is:

$$\Delta G_S = -RTlnK_S \propto_M + RTln\frac{C_M}{[H]^{2m/n}} \quad (28)$$

where $\propto_M$ is determined by the above expressions, (19) or (21).

Thus, within the generalized interaction equations, describing the chemical equilibrium in the "*solid phase – aqueous solution*" system, taking into account the contribution of various secondary reactions, offers several advantages. Firstly, total/global thermodynamic functions can be introduced, thereby determining both the feasibility and optimal conditions of the precipitation - dissolution process. Secondly, the generalized interaction equations explicitly account for the contribution of all species present in the system to the equilibrium state.

2.2. Fundamental mass balance equations within the residual concentration method for multicomponent two-phase systems

Within the framework of the *RC* method [12] and the above deduced generalized equation of integral heterogeneous processes, the key MB equation is written as follows:

$$C_i^0 = C_i^r + \Delta C_i \quad (29)$$

Here, C_i^0 and C_i^r denote the initial and residual concentrations of the ion "i "in the solution, respectively, and ΔC_i represents its amount in the precipitate per Liter of solution. The *MB* equations for the generalized process (24) have the following form:

$$C_M^0 = C_M^r + \Delta C_M \quad (30)$$

$$C_{OH}^0 = C_{OH}^r + \Delta C_{OH} = -C_H^0 \quad (31)$$

Additionally, within the CR method, the following relations are valid:

$$m = \frac{\Delta C_{OH}}{\Delta C_M}, \qquad C_{OH}^0 = -C_H^0, \qquad C_{OH}^r = -C_H^r \tag{32}$$

Taking these relations into account, after transformation, equation (31) takes the form:

$$C_H^0 = -m\Delta C_M + C_H^r \tag{33}$$

The residual concentrations of the ions C_M^r and C_H^r represent the total concentrations in the solution of all species containing ions of the given type:

$$C_M^r = [\mathrm{M}] + \sum_{i=1}[M(OH)_i] = [M]\left(1 + \sum_{i=1}^{m} K_i[H]^{-i}\right) = [M] \propto_M \tag{34}$$

$$C_H^r = [H] - [OH] - \sum_{i=1} i[M(OH)_i] = [H] - [OH] - \sum_{i=1}^{m} iK_i[H]^{-i} \tag{35}$$

In writing the above relations, the equations of the law of mass action [1,5,8] have been used. The degree of complexation is denoted by $\propto_M$, equations (19) or (21). The equilibrium concentration of the metal ion [*M*] is determined from the solubility product and is equal to

$$[M] = K_S[H]^m \tag{36}$$

2.3. Dependence of the precipitation degree of slightly soluble compounds on a series of concentration variables in multicomponent ecosystems

For the quantitative estimation of the precipitation process of compounds from aqueous solutions, various characteristics are used, with solubility *S* being the most frequently employed [13-15]. Solving this type of problem is associated with certain difficulties because, under real conditions, the ions of the precipitate participate in conjugated reactions with both the dissociation products of the solvent (water) and other substances present in the natural waters (as impurities). This leads to a reduction in the fraction of the metal precipitated in the form of slightly soluble compounds. Additionally, in many technological schemes and analytical procedures, a preliminary estimation of the fraction or part of the metal ion precipitated as slightly soluble compounds is necessary, depending on a series of concentration parameters (initial concentration ratios of the components, solution pH, etc.).

As a characteristic of the fraction of the precipitated metal ion, the degree of precipitation can be used:

$$\gamma = \frac{C_M^0 - C_M^r}{C_M^0} \tag{37}$$

Here, C_M^0 and C_M^r denote the total concentration of the metal ion in the mixture and its residual concentration in the solution. The following set of reactions will be examined in the system "*solid phase* $M_mA_{n(S)}$ *- saturated aqueous solution*":

$$M_mA_{n(S)} = mM + nA, \qquad K_S = [M]^m[A]^n \tag{38}$$

$$iM + jH_2O = M_i(OH)_j + jH, \quad K_{ij}[M_i(OH)_j[H]^j/[M]^i \tag{39}$$

$$A + kH = H_kA, \qquad \beta_k = [H_kA]/\left([H]^k[A]\right) \tag{40}$$

In equations (38)-(40), alongside the reaction equations, the respective expressions of the law of mass action are included. For the hydrolysis of the metal ion and the protonation of the anion, the coefficients ∝ are used:

$$\propto_M = \frac{C_M^r}{[M]} = 1 + \sum_i \sum_j iK_{M_{i(OH)_j}}[M]^{i-1}[H]^{-i} \tag{41}$$

$$\propto_A = \frac{C_A^r}{[A]} = 1 + \sum_{k=1} \beta_k[H]^k \tag{42}$$

Between the total concentration of the metal ion C_M^0 and its residual concentration C_M^r in the solution, there exists the reciprocal relationship (29). Noting by *P* the amount of precipitated salt per unit

volume of solution, with the stoichiometry of the precipitate considered, the mass balance conditions can be rewritten as follows:

$$C_M^0 = mP + C_M^r, \qquad C_A^0 = nP + C_A^r \tag{43}$$

The solution of the system of equations (37) and (43) with respect to γ yields

$$\gamma = \frac{mP}{C_M^0} \tag{44}$$

From equations (43) and (44) it results:

$$\gamma = \frac{m}{n}\left(\frac{C_A^0 - C_A^r}{C_M^0}\right), \qquad C_A^r = C_A^0 - \frac{n}{m}\gamma C_M^0 \tag{45}$$

Finally, by combining equations (37) and (45), the following is obtained:

$$K_S^{cond} = \left(C_M^0(1 - \gamma C_M^0)\right)^m \left(C_A^0 - \frac{n}{m}\gamma C_M^0\right)^n, \tag{46}$$

where K_S^{cond} is the conditional solubility product, defined as:

$$K_S^{cond} = (C_M^r)^m (C_A^r)^n = K_S \propto_M^m \propto_A^n \tag{47}$$

Equation (46) constitutes an implicit equation of the function γ in terms of the total concentrations of ions in the mixture C_M^0 and C_A^0 and the pH of the medium. Taking into account relation (45), the final equation can be transformed with respect to γ:

$$\gamma = 1 - \frac{\left(K_S^{cond}\right)^{1/m}}{C_M^0 (C_A^r)^{n/m}} \tag{48}$$

By solving the system of equations (45) and (46), the formula for calculating the function $\gamma = f(pH)$ for fixed values of C_M^0 and C_A^0 is obtained. For example, for m=1, n =2 and $C_A^0 = 2\ C_M^0$, the following mathematical relation is obtained:

$$\gamma^3 - 3\gamma^2 + 3\gamma + \frac{K_S \propto_M \propto_A^2}{2(C_M^0)^2} = 0$$

In the case of the stoichiometric ratio of the total concentrations of the precipitate components in the mixture, i.e., $nC_M^0 = mC_A^0$ (***condition A***), equation (48) takes the form:

$$\gamma = 1 - \frac{1}{C_M^0}\left(\frac{K_S^{cond} m^n}{n^n}\right)^{\frac{1}{m+n}} \tag{49}$$

Thus, when *condition A* is satisfied, the degree of precipitation of the metal ion is calculated using a single equation (49). It should be noted that equations (48) and (49) are applicable only under conditions where thermodynamically the transformation of the salt precipitate $M_m A_{n(S)}$ into slightly soluble hydroxide $M(OH)_{m(S)}$ is impossible, which typically occurs in alkaline environments with high concentrations of the metal ion in solution.

Above, the relationships for calculating thermodynamic functions for the precipitation-dissolution processes of slightly soluble salts were derived. Here, the reciprocal relationship between experimental data obtained through the residual concentration method, solubility, and total thermodynamic functions will be analyzed for the system "*slightly soluble salt - saturated aqueous solution*". The obtained relationships allow for estimating the concentrations of all system components based on the amount of precipitated salt, given a complete set of standard thermodynamic data, and for calculating total thermodynamic functions from experimental data.

The process of formation - dissolution of the slightly soluble salt of composition $M_m A_{n(S)}$, where M^{n+} is the metal ion and A^{m-} is the anion of the salt), according to equation (38), will be examined. Along with the process (38), in a wide range of variation of the pH of the solution, secondary reactions of the salt components (39) and (40) with the dissociation products of the solvent (water) are possible. Based

on the *RC* method, provided that the ion quantity is determined based on the total and residual concentrations, the mass balance equations for the system (38)-(40) take the form (30) and (50):

$$C_A^0 = C_A^r + \Delta C_A = C_A^r + \frac{n}{m}\Delta C_M \quad (50)$$

Under the conditions of reactions (39) and (40), the residual concentrations are defined by equations (41) and (42). At the same time, the expression (23) for the Gibbs energy variation of the integral process (38) - (40) was deduced above. From equations (38), (41) and (42) the equality can be obtained:

$$lnK_s \propto_M^m \propto_A^n = ([M] \propto_M)^m ([A] \propto_A)^n = (C_M^r)^m (C_A^r)^n$$

Then equation (23) can be rewritten as follows:

$$\Delta G_S = -mRTln\frac{C_M^r}{C_M^0} - nRTln\frac{C_A^r}{C_A^0}, \quad (51)$$

or, taking into account (30) and (50)

$$\Delta G_S = -mRTln\frac{(C_M^0 - \Delta C_M)}{C_M^0} - nRTln\frac{(C_A^0 - \Delta C_A)}{C_A^0} \quad (52)$$

From equations (23) and (52) the following relationship for the equilibrium constant can be obtained

$$K_S = \left(\frac{C_M^r}{\propto_M}\right)^m \left(\frac{C_A^r}{\propto_A}\right)^n$$

The coincidence of the ΔG_S values, determined from experimental data according to equation (52) with the values, calculated using equation (23), serves as proof of the correctness of the selected equilibrium model. If these values differ, it can be summarized regarding the incomplete record of all possible equilibria (39) and (40). Thus, the expressions obtained show that the experimental data of the *RC* method can be expressed by the thermodynamic functions of the integral process (38) - (40).

The derived expressions also allow establishing a principled possibility of determining the total thermodynamic characteristics from the experimental data, obtained by means of the *RC* method. At the same time, in the presence of a complete set of thermodynamic functions of all possible reactions (38) - (40) it is possible to estimate the amount of precipitate depending on the initial concentrations of the ion concentrations in the mixture and the pH of the solution.

From the above, it becomes obvious that the obtained relationships have both theoretical and practical importance in the research of systems that contain solid phases. The obtained results once again confirm the necessity and importance of the experimental determination of the standard thermodynamic characteristics of precipitation, hydrolysis and complexation reactions in solutions [13-17]. The calculation of functions (17), (23), (51) and (52) for a series of real systems according to the equations derived in this work proved their veracity [2,5,8,10].

3. CONCLUSIONS

This study presents a robust framework that effectively integrates unique mass balance equations for soluble and insoluble species in heterogeneous natural aqueous ecosystems, specifically focusing on two-phase systems comprising a solid phase as a mineral and a saturated multicomponent aqueous ecosystem. By introducing fundamental mass balance equations within the residual concentration method, the research successfully investigates the thermodynamic functions of various chemical interactions in aqueous ecosystems, including metal ion hydrolysis, ligand protonation, and complex formation as described by a generalized reaction equation.

The innovative approach allows for the estimation of solid phase quantities based on the initial composition of the mixture and the solution pH, and it can be extended to more complex systems involving additional reactions. The advanced thermodynamic model demonstrates strong agreement with existing experimental findings, validating its applicability to real-world aquatic systems.

The relationships derived in this study have broad applications, including optimizing conditions for transforming one solid phase (mineral) into another, synthesizing chemical substances through precipitation methods, enhancing coprecipitation techniques, and improving fractional precipitation from homogeneous solutions. This framework provides valuable insights and tools for addressing a variety of challenges in the management and conservation of aquatic ecosystems.

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