

# THERMODYNAMIC CALCULATIONS OF COMPLEX CHEMICAL EQUILIBRIA IN SOILS CONTAINING ALUMINIUM MINERALS

## CALCULE TERMODINAMICE ALE ECHILIBRELOR CHIMICE COMPLEXE ÎN SOLURI CARE CONȚIN MINERALE DE ALUMINIU

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**Abstract.** A thermodynamic method for calculating complex chemical equilibria in soils containing aluminium minerals under the real, non-standard conditions has been developed. The expression for calculating the change in real Gibbs energy was deducted. Heterogeneous systems with simultaneous reactions involving aluminium soluble and insoluble (minerals) species have been investigated. Comparisons of thermodynamic stability of Al oxysulfate minerals and gibbsite were carried out. The developed approach for calculating the Gibbs energy may be successfully applied for the prediction of complex chemical processes in soil.

**Key words:** aluminium minerals, complex formation, Gibbs energy, thermodynamic stability.

**Rezumat.** A fost elaborată o metodă termodinamică de calcul ale echilibrelor chimice complexe în soluri care conțin minerale de aluminiu în condiții reale, diferite de cele standard. S-a dedus expresia de calcul a energiei Gibbs în condiții reale. Au fost studiate sisteme eterogene cu participarea speciilor solubile și insolubile (minerale) ale ionului de aluminiu. S-a efectuat o comparație a stabilității termodinamice a mineralelor de oxisulfat de aluminiu cu gibbitul. Metoda elaborată de calcul a energiei Gibbs poate fi aplicată cu succes pentru prezicerea unui șir de procese chimice complexe în sol.

**Cuvinte cheie:** energia Gibbs, formarea complexilor, minerale de aluminiu, stabilitatea termodinamică.

### INTRODUCTION

Soils are open heterogeneous (multiphase) multicomponent systems in which a large number of mutually dependent chemical reactions take place with involvement of the soil biota as well. The physicochemical complexity of soils, the main characteristics of their chemical behavior can be understood on the basis of thermodynamic principles and methods of research of the complex chemical reactions in aqueous heterogeneous systems. In this paper, the mathematical expressions for calculating the Gibbs energy for systems “aluminium mineral (solid phase) – aqueous saturated solution”, in the presence of a series of chemical species that react with the  $\text{Al}^{3+}$  ions, especially in acid soil solutions, have been derived.

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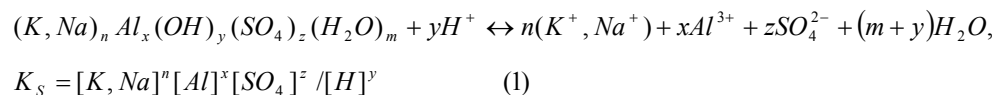
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In aqueous media aluminum can be found in a variety of soluble and insoluble forms. The high concentrations of aluminum may affect the buffer capacity and transport of elements in aquatic ecosystems, this element being toxic for aquatic organisms. Although understanding the chemistry and effects of aluminum in aqueous environment has substantially increased in recent years, some additional researches are required to identify the sources of aluminum and mechanisms of its transport from the soil solution to ground surface waters in order to assess the effects of aluminium on phosphorus compounds, trace metals and organic carbon cycle, as well as the action of different aluminum-containing species on aquatic organisms. Ecologically significant concentrations of aluminum were identified in surface waters due to acidic deposition. Mineral acids derived from rainfalls mobilize aluminium from minerals formed as a result of the soil evolution, which is transported to the adjacent surface waters.

The soluble aluminium in soil solutions is found as the  $Al^{3+}$  ions along with chemical combinations with  $OH^-$ ,  $F^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$  and organic compounds. Although the recent investigations have often ignored the presence of aluminum non - hydroxylic complexes, it can be assumed that the complex organic species and fluorides are the predominant forms of aluminum in dilute acidic surface waters (with a low ionic strength). The concentration of inorganic aluminum forms increases exponentially with decreasing the pH of solution. This phenomenon is analogous to the theoretical dependence of the solubility of mineral phases on pH values. At the same time, the concentration of organic aluminium species correlates better with the variations in the organic carbon concentration from surface waters than with the environmental pH. High concentrations of aluminum in dilute acidic waters are of interest from several points of view: aluminium is an important buffer of pH; aluminum can influence the cycle of important elements, such as phosphorus, organic carbon and metal ions; aluminum is potentially toxic to aquatic organisms.

## THEORETICAL PART

As insoluble species of aluminium a series of minerals with general composition  $(K, Na)_n Al_x (OH)_y (SO_4)_z (H_2O)_m$  has been investigated. Their solubility can be controlled by the following dissolution-precipitation equilibrium:



where  $K_s$  is the solubility product of aluminium mineral. The ionic charges and influence of ionic strength are omitted for simplicity.

The  $Al^{3+}$  concentration can be calculated from the  $K_s$  expression (1):

$$[Al] = K_s^{1/x} [K, Na]^{-n/x} [SO_4]^{-z/x} [H]^{y/x}. \quad (2)$$

In this paper the following mineral have been investigated: 1) jurbanite  $Al(OH)(SO_4) \cdot 5(H_2O)$ , 2) basaluminite  $Al_4(OH)_{10}(SO_4) \cdot 5(H_2O)$ , 3) alunite  $KAl_3(OH)_6(SO_4)_2$ , 4) alunogel  $Al_2(SO_4)_3 \cdot 17(H_2O)$  and 5) gibbsite  $Al(OH)_3$ . Concomitantly with the process (1) a large set of possible equilibria in the system „mineral – soil solution” has been considered. In the soil solution  $Al$  is found in different soluble forms, including  $Al^{3+}$  and its hydroxo, fluoride, sulfate and organic complexes. There are also the phosphate complexes and polymeric species of aluminium. Iron (III) forms with the  $Org^{3-}$  ligand two complexes. As polynuclear species of aluminium, the dimer  $Al_2(OH)_2^{4+}$  and trimer  $Al_3(OH)_4^{5+}$  have been taken into account. The polymeric species with the great molecular masses  $Al_i(OH)_j^{3i-j}$ , where  $i = 6, 8$  and  $13$  are not examined since they practically are not formed in the soil solution due to the low polymerization kinetics. At the same time, the organic acids in soil solution inhibit their formation (Povar and Rusu, 2012). The phosphate complexes of aluminum can be presented as  $AlH_2PO_4^{2+}$ . The silicate complexes of aluminium are ignored because of their weak complexation properties. The mass balance (MB) conditions in the examined systems have been formulated within the method of residual concentrations (RC) (Povar, 1994; Povar, 1997):

$$C_{Al}^0 = C_{Al}^r + \Delta C_{Al} = \sum_{i=1} \sum_{j=0} i[Al_i(OH)_j^{3i-j}] + \sum_{j=1} [AlF_j^{3-j}] + [AlSO_4^+] + [Al(SO_4)_2^-] \quad (3)$$

$$+ [AlOrg^0] + [AlHOrg^+] + [AlH_2PO_4^{2+}] + \Delta C_{Al}$$

$$C_F^0 = [F^-] + [HF^0] + \sum_{j=1} j[AlF_j^{3-j}] = [F^-] + K_{HF}[H^+][F^-] + K_S[H^+]^3 \sum_{j=1} jK_{f,j}[F^-]^j \quad (4)$$

$$C_{SO_4}^0 = [SO_4^{2-}] + [AlSO_4^+] + 2[Al(SO_4)_2^-] + \Delta C_{SO_4} \quad (5)$$

$$C_{Org}^0 = \sum_{m=0} [H_mOrg^{m-3}] + [AlHOrg^+] + [AlOrg^0] \quad (6)$$

$$C_{PO_4}^0 = \sum_{l=0} [H_lPO_4^{l-3}] + [AlH_2PO_4^{2+}] \quad (7)$$

$$C_K^0 = [K^+] + \Delta C_K \quad (8)$$

$$C_H^0 = C_H^r + \Delta C_H = [H^+] - [OH^-] - \sum_{i=1} \sum_{j=1} j[Al_i(OH)_j^{3i-j}] + [AlHOrg^+] + 2[AlH_2PO_4^{2+}] + [HF^0] + \\ + \sum_{m=1} m[H_mOrg^{m-3}] + [HCO_3^-] + 2[H_2CO_3^0] + \sum_{l=1} l[H_lPO_4^{l-3}] + \Delta C_H \quad (9)$$

The quantities  $C_i^0$  and  $C_i^r$  (mol/L) in equations (3)-(8) represent respectively the analytical and residual concentrations of component  $i$  in the heterogeneous system, while  $\Delta C_i$  symbolizes its quantity in the precipitate in one liter of solution (Povar, 1997). Within the RC method, the relations  $\Delta C_{OH} = -\Delta C_H$  and  $C_{OH}^r = -C_H^r$  are applicable. In the

equation (9)  $C_H^0$  denotes the excess of  $H^+$  ions versus hydroxyl ions in biphasic mixtures,  $C_H^0 = -C_{OH}^0$  [4]. From the stoichiometric composition of minerals of type  $(K, Na)_n Al_x (OH)_y (SO_4)_z (H_2O)_m$  the following relations are derived:

$$\frac{1}{y} \Delta C_{OH} = \frac{1}{z} \Delta C_{SO_4} = \frac{1}{n} \Delta C_K = \frac{1}{x} \Delta C_{Al}. \quad (10)$$

The equilibrium concentration of ion  $Al^{3+}$  is determined from the relation (2). From the MB equations BM (3)-(8) for a certain pH value, taking into account the relations (10) and the equations of the law of mass action (LMA), one can obtain a system of five nonlinear equations (or 6 equations, in the case of alunite  $KAl_3(OH)_6(SO_4)_2$ ) with 5 or 6 variables, respectively  $[F]$ ,  $[Org]$ ,  $[SO_4]$ ,  $[PO_4]$ ,  $\Delta C_i$  and  $[K^+]$ , that can be easily solved by computerized numerical methods (Povar, 1994; Povar, 1998; Povar, 2000; Povar, 2001). Then, the residual concentrations of the component  $i$  are calculated,  $C_i^r$ , knowing the initial composition of heterogeneous mixture, e.g. the quantities  $C_i^0$ .

Within the thermodynamic approach, previously developed (Fishtik et al., 1986; Fishtik and Povar, 1987; Fishtik et al., 1987; Fishtik et al., 1989; Povar, 1994; Povar and Rusu, 2012) and extended in this paper for the solid phases with a more complex composition, it has been demonstrated that the values of the total Gibbs energy  $\Delta G_{S,tot}$  for the examined complex processes, where a large set of simultaneous reactions take place, can be calculated by the following equation:

$$\Delta G_{S,tot} = -xRT \ln \frac{C_{Al}^r}{C_{Al}^0} - zRT \ln \frac{C_{SO_4}^r}{C_{SO_4}^0} - nRT \ln \frac{C_K^r}{C_K^0} \quad (11)$$

In order to compare the  $\Delta G_{S,tot}$  values for different minerals, the Gibbs energy referred to one mole of aluminium,  $\Delta G'_{S,tot}$ , has been calculated:

$$\Delta G'_{S,tot} = -RT \ln \frac{C_{Al}^r}{C_{Al}^0} - \frac{z}{x} RT \ln \frac{C_{SO_4}^r}{C_{SO_4}^0} - \frac{n}{x} RT \ln \frac{C_K^r}{C_K^0} \quad (12)$$

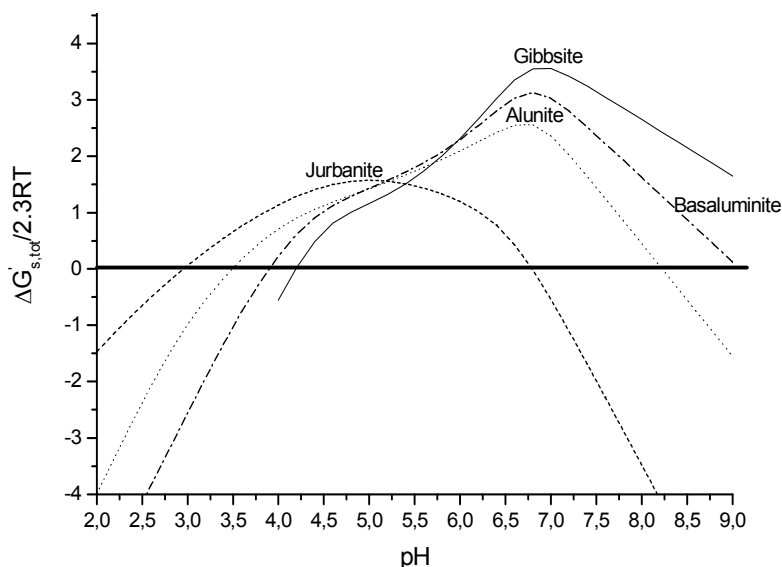
The solid phase  $(K, Na)_n Al_x (OH)_y (SO_4)_z (H_2O)_m$  is stable if  $\Delta G_{S,tot} > 0$ . The condition  $\Delta G_{S,tot} = 0$  corresponds to the beginning of mineral dissolution/precipitation.

## RESULTS AND DISCUSSIONS

Fig. 1 shows the variation of the Gibbs energy versus pH in the "aqueous saturated solution - mineral" systems for different concentrations of individual components. This proves that the aluminium residual concentration can vary

within the large limits for the same pH value. Therefore, the pH value is not the exclusive factor controlling the soluble aluminium concentration.

The analysis of obtained data shows that the thermodynamic stability areas of studied soil minerals become considerably larger at increasing total (analytical) concentrations. Calculations also show that significant amounts of inorganic ligand  $F^-$ , as well as organic ligand  $Org^{3-}$  affect significantly the solubility of minerals. Under the examined conditions alunogel is thermodynamically unstable.



**Fig. 1.** - Gibbs energy versus pH of soil solution ( $C_{Al}^{3+} = 1 \times 10^{-3}M$ ,  $C_{SO_4^{2-}} = 1 \times 10^{-3}M$ ,  $C_{F^-} = 5 \times 10^{-6}M$ ,  $C_{Org} = 10^{-4}M$ ,  $C_{PO_4} = 10^{-4}M$ )

For high concentrations of the aluminum and sulfate ions  $C_{Al}^0 = C_{SO_4}^0 = 1 \cdot 10^{-3}M$  (Fig. 1) and different pH values, the condition  $\Delta G_{S,tot} > 0$  occurs for all the minerals, except for alunogel. In Fig. 1 one can identify the pH areas in which the aluminium minerals are thermodynamically stable: alunite (3.2 ÷ 8.6), basaluminite (4.0 ÷ 9.0), gibbsite (4.2 ÷ 10.6) and jurbanite (3.0 ÷ 6.8). Furthermore, the maximal thermodynamic stability of minerals varies as a function of the pH of heterogeneous mixtures. In the pH area of 3.0 ÷ 5.0 the most stable mineral is jurbanite, then for the pH values of 5.2 ÷ 5.8 is basaluminite, and for the pH values greater than 6.0 is gibbsite.

The obtained data, based on thermodynamic calculations, explain the following experimental results: (a) the increase in sulfate concentration in soil solutions leads to a considerable decrease of the aluminium residual concentration and (b) high concentrations of  $SO_4^{2-}$  and basic cations play an important detoxification role for aquatic organisms (Bi et al., 2001).

## CONCLUSIONS

1. A thermodynamic method for calculating complex chemical equilibria under the real conditions in soils containing aluminium minerals has been developed. The mass balance equations, derived within the method of residual concentrations, take explicitly into account all the soluble and insoluble chemical species in biphasic systems “mineral – soil solution”.

2. The expression for the variation of Gibbs energy under real, non-standard conditions has been derived.

3. The areas of thermodynamic stability of different aluminium-containing minerals with the general composition  $(K, Na)_n Al_x (OH)_y (SO_4)_z (H_2O)_m$  have been determined for a large area of pH variation and different values of aluminium and sulfate concentrations. The obtained data fitted well with the experimental data previously obtained.

4. The thermodynamic method developed and used in this paper contributes to elucidate the mechanism of controlling aluminum concentration in dilute acid soil solutions.

5. The developed approach for calculating the Gibbs energy may be successfully applied for the prediction of complex chemical processes in soil.

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