THERMODYNAMIC ANALYSIS OF HETEROGENEOUS EQUILIBRIA IN NATURAL WATERS

Igor Povar and Oxana Spinu

Abstract: A thermodynamic approach for calculating heterogeneous equilibria in natural waters has been developed. The overall heterogeneous processes in the "solid phase – aqueous solution" system have been described by the generalized equation of reactions, where the soluble species are thought to be formed in quantities proportional to their molar fractions. The developed method for calculating the Gibbs energy has been successfully used for describing chemical processes in natural waters. The developed method is general and can be applied to all heterogeneous processes in aquatic systems involving one or several solid phases.

Keywords: Gibbs energy, heterogeneous equilibria, thermodynamic analysis.

Introduction:

It is well-known that soil minerals are the primary source of *Al* to aqueous environments. For example, in the lithosphere, *Al* is largely associated with highly crystalline alumino-silicate minerals. A possible cycle of *Al(III)* in natural waters involves aluminum minerals, dissolved monomeric species, dissolved and aggregated polymers. The hydrolysis and complex formation reactions in aqueous solution produce a large variety of organic and inorganic aluminum species and can influence the precipitation of solid aluminum phases (Tipping et al. 1995). Models based on equilibrium thermodynamics have been

the most commonly used approach to predicting Al quantities in aqueous solutions.

The magnitude of errors in predicting (Al^{3+}) has important implications for plant growth. In nutrient solutions, the activities of Al^{3+} as low as 2 μM are toxic to barley (Cameron et al. 1986). The most toxic *Al* species is widely considered to be the Al^{3+} ion and, to a lesser extent, monomeric hydroxy-aluminium species; in contrast, stable AlF_x complexes are not considered phytotoxic (Hammond et al. 1995). On the other hand, the acid deposition currently affects large areas of the earth. Long-term prediction of the complex chemical processes and their practical consequences is only feasible by using simulation models. Thus, it is of interest to calculate the change in Gibbs energy under real conditions, ΔG, in order to find out how much this change differs from the quantity ΔG^0 under standard conditions. Such sort of problems were extensively examined in (Fishtik and Povar 1987; Fishtik et al. 1987; Povar et al. 1989; Povar 1994, 1997; Povar and Rusu 2012).

Igor Povar and **Oxana Spinu:**
Institute of Chemistry
Academy of Sciences of Moldova
Academiei no. 3, Chișinău
MD 2028, Republic of Moldova
e-mail:
Igor Povar: ipovar@yahoo.ca
Oxana Spinu: oxana_spinu@yahoo.com
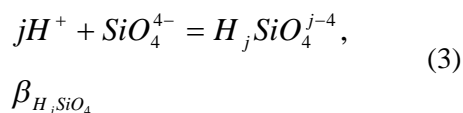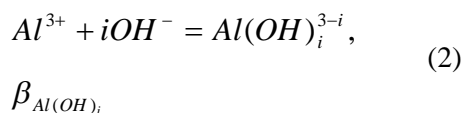
Materials and methods:

Theory and calculations

Firstly, the equilibrium between a mineral, for example, kaolinite, as a common aluminum silicate mineral, and an aqueous solution will be considered. This equilibrium is usually described by the Eq. (1):
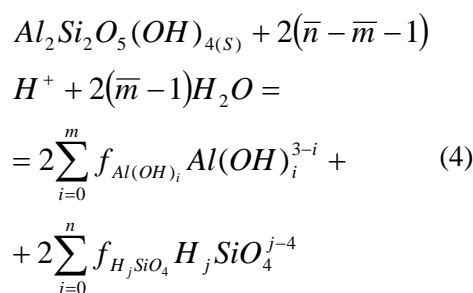
$$Al_2Si_2O_5(OH)_{4(S)} + 6H^+$$
$$\leftrightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O \qquad (1)$$
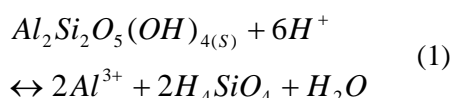
The standard Gibbs energy of this reaction is $\Delta G_r^0 = $ -43.5 kJ/mol (Sposito 1989). Therefore, under standard conditions, the equilibrium (Eq. 1) is shifted to the right side. Secondly, the (Eq. 1) describes correctly the equilibrium between kaolinite and the aqueous solution only in acidic solutions, where the aluminum ion Al^{3+} does not undergo hydrolysis and the orthosilicic acid H_4SiO_4 is nondissociated. By rising the pH, the hydrolysis of Al^{3+} as well as the dissociation of H_4SiO_4 intensify. Therefore, the form of (Eq. 1) changes with the increase of the pH.

For the sake of convenience, the formation of hydroxocomplexes $Al(OH)_i^{3-i}$ (instead of the Al^{3+} hydrolysis) and protonated species $H_jSiO_4^{j-4}$ (in place of the orthosilicic acid dissociation) will be considered (Eqs. 2, 3):

$$Al^{3+} + iOH^- = Al(OH)_i^{3-i},$$
$$\beta_{Al(OH)_i} \qquad (2)$$

$$jH^+ + SiO_4^{4-} = H_jSiO_4^{j-4},$$
$$\beta_{H_jSiO_4} \qquad (3)$$

where $\beta_{Al(OH)_i}$ and $\beta_{H_jSiO_4}$ are the overall thermodynamic constants of corresponding species formation.

In order to take into account all the chemical species formed by (2) and (3), it is necessary to obtain a generalized equation of the complex process involving reactions (1)-(3). For this purpose, following (Fishtik and Povar 1987; Fishtik et al. 1987) the equilibria in the "kaolinite – aqueous solution" system can be described by the generalized equation of the reactions:

$$Al_2Si_2O_5(OH)_{4(S)} + 2(\bar{n} - \bar{m} - 1)$$
$$H^+ + 2(\bar{m} - 1)H_2O =$$
$$= 2\sum_{i=0}^{m} f_{Al(OH)_i} Al(OH)_i^{3-i} + \qquad (4)$$
$$+ 2\sum_{j=0}^{n} f_{H_jSiO_4} H_jSiO_4^{j-4}$$

Here $f_{Al(OH)_i}$ and $f_{H_jSiO_4}$ are the partial molar fractions of the species $Al(OH)_i^{3-i}$ and $H_jSiO_4^{j-4}$ respectively, while $\bar{m}$ and $\bar{n}$ are Bjerrum functions, defined by the relations:

$$\bar{m} = \sum_{i=1}^{m} i f_{Al(OH)_i}, \quad \bar{n} = \sum_{j=1}^{n} j f_{H_jSiO_4} \quad (5)$$

During the deduction of (Eq. 4) it was taken into account that the species $Al(OH)_i^{3-i}$ and $H_jSiO_4^{j-4}$ are formed in quantities proportional to their partial molar fractions. Such supposition permits to take rigorously into account the mass balance in (Eq. 4). Under standard conditions, the following expression for ΔG_r^0 is obtained:

$$\Delta G_r^0 = -RT \ln K_r \prod_{=1}^{m} \beta_{Al(OH)_i}^{2f_{Al(OH)_i}} \tag{6}$$

$$\prod_{j=1}^{n} \beta_{H_jSiO_4}^{2f_{H_jSiO_4}} \beta_{H_2O}^{-2\overline{m}}$$

The change in the Gibbs energy of the reactions (Eq. 4) under real, non-standard conditions derived in this paper, takes the form:

$$\Delta G_r = -RT \ln K_r \alpha_{Al}^2 \alpha_{Si}^2 + \\ + RT \ln C_{Al}^2 C_{Si}^2 \tag{7}$$

It is easy to deduct that the logarithmic expression of the first term in (Eq. 7) represents the conditional solubility product $K_S^{cond} = K_r \alpha_{Al}^2 \alpha_{Si}^2$ (Fishtik et al. 1987). So, for $C_{Al} = C_{Si} = 1$ mol/L, ΔG_r is directly related to the K_S^{cond} value.

Results and discussion:

In Figure 1 there are depicted the obtained results for calculating ΔG_r^0 and ΔG_r, as a function of pH according to (Eqs. 6, 7) for $C_{Al} = C_{Si} = 1$ mol/L. As one can see, the calculations of the function ΔG_r (pH) in the linear approximation leads to rather acceptable results. For ΔG_r^0, however, this approximation is much worse.

The analyzed example shows sufficiently convincing that the change in Gibbs energy under real conditions can differ essentially from the standard value, and therefore, the conclusions made on the basis of the ΔG_r^0 values are not always acceptable. Figure 2 gives some examples of the calculated ΔG_r (pH) dependence for the "mineral-aqueous solution" system. Hence, by solving the questions associated with the thermodynamic possibility of the occurrence of natural waters processes, the preference

should be given to calculating the change in Gibbs energy under real, specific conditions. The sign of the "real" Gibbs energy effect and, respectively, the direction of overall process depend strongly on pH values.

In natural waters a number of different anions is presented owning a great complex formation capacity towards metal ions. Within the framework of the developed approach, the account of complex formation is effectuated analogously. For better lucidity, the calculation of the change in Gibbs energy dependence on pH for the "kaolinite-aqueous solution" system in the presence and absence of fluoride ion is examined below. The latter forms quite stable soluble Al complexes, combining with much more Al when they are present in proper concentrations. In this case, besides the equilibria (Eqs. 2, 3), it is also necessary to take into account the reactions:

$$Al^{3+} + kF^- = AlF_k^{3-k}$$
$$F^- + H^+ = HF$$
$$2F^- + H^+ = HF_2^+$$
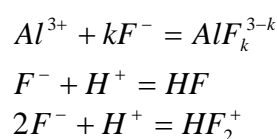
The thermodynamic analysis of equilibria in this system shows that for the change in Gibbs energy under the given conditions the (Eq. 7) is true, in which α_{Al} is a function of fluoride ion concentration as well:

$$\alpha_{Al} = 1 + \sum_{i=1}^{m} \beta_{Al(OH)_i} [OH]^i + \\ + \sum_{k=1}^{p} \beta_{AlF_k} [F^-]^k \tag{8}$$

Here $[F^-]$ is the equilibrium concentration of fluoride ion, which is computed from the mass balance condition of the fluoride ion. Figure 3 shows that the fluoride ion has a substantial influence on the equilibrium in the system of kaolinite-aqueous solution. In particular, in the presence of fluoride ions the thermodynamic area of the kaolinite stability narrows

considerably. Therefore, fluoride maintains higher concentrations of *Al* than might be expected from mineral solubility equilibria, particularly at pH 5–9, that confirms the experimental data obtained earlier (Fishtik and Vataman 1988).

Figure no. 1   pH dependence on Gibbs energy for the system of kaolinite-aqueous solution under standard (1) and nonstandard state conditions (2). (Continuous lines – exact calculations according to (Eq. 7); broken lines: calculation by (Eq.6)).
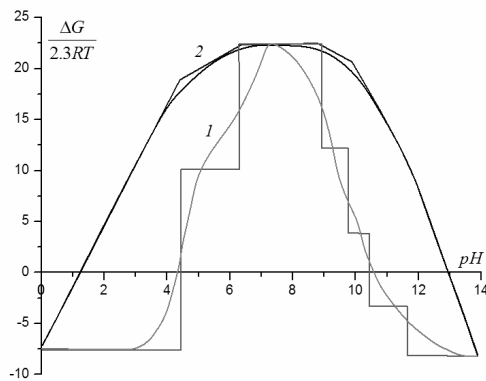

Figure no. 2   Relation of ΔGr to pH for a number of aluminosilicates at $C_{Al} = C_{Si} = 1·10^{-3}$ mol/L. 1 – andalusite; 2 – gibbsite; 3 – pyrofillite; 4 – kaolinite.
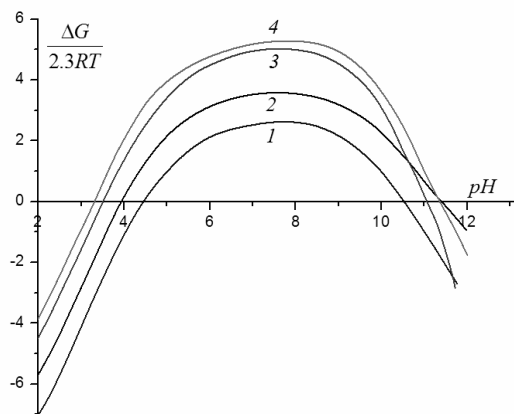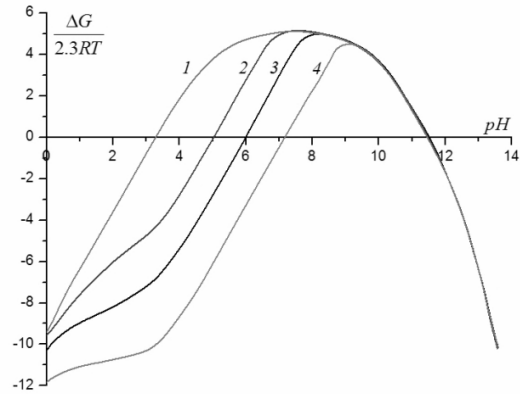

Figure no. 3   The influence of fluoride ion concentration on the change in Gibbs energy for the system of kaolinite-aqueous solution at the total fluoride concentration, mol/L: 1 – 0; 2 - $1·10^{-4}$; 3 - $1·10^{-3}$; 4 - $1·10^{-2}$.

Conclusions:

A thermodynamic method for calculating mineral equilibria in natural waters has been developed. The chemical equilibrium processes in the system of "mineral – aqueous solution" have been described by the generalized equation of reactions, where the aqueous soluble species are supposed to be formed in amounts proportional to their partial molar fractions. The mathematical expressions for calculating the change in Gibbs energy of the overall processes, taking into account such side reactions as hydrolysis and complex formation under real, non-standard conditions, have been deduced. There has been elucidated the physical meaning of the conditional solubility product. The developed approach for calculating the Gibbs energy has been successfully applied for chemical processes in natural waters. This method is universal and can be applied for all heterogeneous processes in aquatic systems involving one or several solid phases.

Rezumat:

ANALIZA TERMODINAMICĂ A
ECHILIBRELOR HETEROGENE
ÎN APELE NATURALE

S-a dezvoltat o abordare termodinamică pentru calcularea echilibrelor heterogene în apele naturale. Procesele heterogene în sistemul de "fază solidă – soluție apoasă" au fost descrise prin ecuația generalizată a reacțiilor, unde se consideră că speciile solubile s-au format în cantități proporționale cu fracțiile lor molare. Metoda dezvoltată pentru calcularea energiei Gibbs a fost folosită cu succes pentru descrierea proceselor chimice în apele naturale. Metoda prezentată este generală și poate fi aplicată tuturor proceselor heterogene din sistemele acvatice, implicând una sau câteva faze solide.

References:

CAMERON R.C., RITCHIE G.S.P., ROBSON A. D. (1986), Relative toxicities of inorganic aluminum complexes to barley, *Soil Science Society. Am. J.* 50: 1231-1236.

FISHTIK I., POVAR I. (1987), Side reactions in calculating the thermodynamic functions for the process of formation – dissolution of salt precipitates, *Russ. J. Gen. Chem.* 5: 25 - 30 (Engl. transl.).

FISHTIK I., POVAR I., VATAMAN I. (1987), Thermodynamics of complex chemical equilibria in the system "precipitate of salt – aqueous solution". The formation of polynuclear species, *Zh. Obshch. Khim.* 57: 736-742 (in Russian).

FISHTIK I., VATAMAN I. (1988), *Thermodynamics of Hydrolysis of Metal Ions*, Știința, Chișinău.

HAMMOND K., DAVID E., MARTIN J. (1995), Seed size of woody plants in relation to disturbance, dispersal, soil type in wet neotropical forests, *Plant and Soil* 173: 89-95.

POVAR I. (1994), Thermodynamic calculation of the minimum solubility pH of slightly soluble oxides and hydroxides in polynuclear hydrolysis of metal ion, *Ukr. Khim. Zh.* 60: 371 (in Russian).

POVAR I. (1997), Method for graphic representation of heterogeneous chemical equilibria in systems sparingly soluble compound-complexing agent-aqueous solution, *Russ. J. Inorg. Chem.* 42: 607-612 (Engl. transl.).

POVAR I., FISHTIK I., VATAMAN I. (1989), Calculation of optimal conditions of underground leaching of uranium ores, *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk* 5: 57-61 (in Russian).

POVAR I., RUSU V. (2012), Aluminium heterogeneous speciation in natural waters, *Can. J. Chem.* 290 (4): 326- 332.

SPOSITO G. (1989), *The Chemistry of Soils,* Oxford University Press, New York.

TIPPING E., BERGGREN D., MULDER J., WOOF C. (1995), Modelling the solid–solution distributions of protons, aluminium, base cations and humic substances in acid soils, *European Journal of Soil Science* 46: 77–94.