

Thermodynamic Stability of Chemical Species in Multiple Reaction Systems

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A general thermodynamic and stoichiometric method, recently developed by us to study subtle forms of stability/instability relations among chemical species, such as resonance and strain energies (Fishtik, I.; Datta, R. *J. Phys. Chem. A* **2004**, 108, 5727–5739), is extended to stability relations in multiple chemical reaction systems. Namely, a new definition as well as a new algorithm of evaluation of the stabilities of chemical species, referred to as the overall stabilities, is proposed. It is further shown that the overall stabilities may be partitioned into a sum of contributions associated with a complete set of stoichiometrically unique response reactions (RERs). This finding reveals that the conventional stability analysis is stoichiometrically and thermodynamically inconsistent in that it involves only a part of RERs.

Introduction

Graphical methods of evaluation of thermodynamic stabilities of chemical species in multiple chemical reaction systems are often used in various areas to solve a large variety of problems.^{1–11} The conventional procedure may be summarized briefly as follows. A set of chemical reactions, involved in a combinatorial manner the species whose stability is sought, is generated. Next, an equation for the Gibbs free-energy change as a function of the variables that govern the position of chemical equilibrium is derived for each of these reactions. Finally, the Gibbs free energies of the reactions are set equal to zero, and the obtained equations are solved for stability boundaries of the dominant species. The stability boundaries of the dominant species are normally depicted graphically as 2D or 3D graphs, thus resulting in graphical constructions that are known as predominance or stability diagrams. For instance, the graphical 2D construction comprising the stability boundaries of the species in the coordinates E (potential) – pH is known as a Pourbaix diagram² and is used in rationalizing the thermodynamic behavior of electrochemical systems. The graphical methods of stability analysis were also implemented in commercial software.^{9–10}

Recently,¹² we developed a general thermodynamic and stoichiometric approach to the stability of chemical species aimed to evaluate subtle forms of stability/instability relations of chemical species, such as aromatic stabilization and strain energies. Here, we show that this general method can be extended so as to treat stability relations in multiple chemical reaction systems. Our approach not only provides a remarkable interpretation and an algorithm for evaluation of the species stabilities but also clearly shows the limitations and thermodynamic inconsistency of the conventional graphical methods of stability analysis. At this earlier stage, it should be mentioned that in this work the stability relations among chemical species are considered exclusively in terms of the stoichiometric approach to the chemical equilibrium, i.e., the approach based on the substitution of the mass balance conditions with an arbitrary set of chemical reactions.¹³ It is within this approach

that the conventional stability analysis of the species is performed in a thermodynamically inconsistent way. The use of the nonstoichiometric approach, i.e., the approach based on the direct minimization of the Gibbs free energy subject to mass balance conditions, never leads to errors in the stability analysis.

Notation and Definitions

We consider a system comprising a set of n chemical species B_i ($i = 1, 2, \dots, n$) at a given temperature (T), pressure (P), and species activities a_i ($i = 1, 2, \dots, n$). Let $G_i(T, P, a_1, a_2, \dots, a_n)$ ($i = 1, 2, \dots, n$) be the partial Gibbs free energy of the species. Further, let ϵ_{ij} ($i = 1, 2, \dots, n; j = 1, 2, \dots, s$) be the number of elements E_j ($j = 1, 2, \dots, s$) in the species B_i , where “elements” is meant as any appropriate compositional or structural unit from which the species can be build. It is thus convenient to define the vectors

$$\mathbf{B} = (B_1, B_2, \dots, B_n)^T \quad (1)$$

$$\mathbf{E} = (E_1, E_2, \dots, E_s)^T \quad (2)$$

$$\bar{\mathbf{G}} = (\bar{G}_1, \bar{G}_2, \dots, \bar{G}_n)^T \quad (3)$$

We define further the so-called formula matrix¹³

$$\epsilon = \begin{bmatrix} \epsilon_{11} & \epsilon_{12} & \dots & \epsilon_{1s} \\ \epsilon_{21} & \epsilon_{22} & \dots & \epsilon_{2s} \\ \dots & \dots & \dots & \dots \\ \epsilon_{n1} & \epsilon_{n2} & \dots & \epsilon_{ns} \end{bmatrix} \quad (4)$$

so that

$$\mathbf{B} = \epsilon \mathbf{E} \quad (5)$$

It is assumed that the “elements” are linearly independent, that is, $\text{rank } \epsilon = s$.

Next, we define and generate an arbitrary set of linearly independent chemical reactions involving species B_i ($i = 1, 2, \dots, n$)

$$\rho = \nu \mathbf{B} = 0 \quad (6)$$

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where ρ is the reaction vector

$$\rho = (\rho_1, \rho_2, \dots, \rho_m)^T \quad (7)$$

and ν is the stoichiometric matrix

$$\nu = \begin{bmatrix} \nu_{11} & \nu_{12} & \dots & \nu_{1n} \\ \nu_{21} & \nu_{22} & \dots & \nu_{2n} \\ \dots & \dots & \dots & \dots \\ \nu_{m1} & \nu_{m2} & \dots & \nu_{mn} \end{bmatrix} \quad (8)$$

where ν_{ji} ($j = 1, 2, \dots, m$; $i = 1, 2, \dots, n$) is the stoichiometric coefficient of species B_i in reaction ρ_j . The reactions, i.e., the stoichiometric matrix ν , are generated by solving the mass-balance conditions

$$\nu\epsilon = 0 \quad (9)$$

As well-known from linear algebra, the number of linearly independent solutions of eq 9, i.e., the number of linearly independent reactions ρ , is equal to $m = p - \text{rank } \epsilon = n - s$.

Finally, we define the vector

$$\Delta G = (\Delta G_1, \Delta G_2, \dots, \Delta G_m)^T \quad (10)$$

where ΔG_j ($j = 1, 2, \dots, m$) is the Gibbs free-energy change of the reactions ρ_j ($j = 1, 2, \dots, m$) and is given by

$$\Delta G_j = \Delta G_j^0(T, P) + RT \ln \prod_{i=1}^n a_i^{\nu_{ji}} \quad (j = 1, 2, \dots, m) \quad (11)$$

According to chemical thermodynamic¹⁴ vectors, ΔG and \bar{G} are interrelated via

$$\Delta G = \nu \bar{G} \quad (12)$$

Conventional Stability Analysis

Within the conventional approach, the stability boundaries between species are determined based on Gibbs energy changes ΔG_j ($j = 1, 2, \dots, p$) of individual reactions ρ_j ($j = 1, 2, \dots, p$). These reactions are generated so as to involve in a combinatorial manner all pairs of a given subset of species. The species stability boundaries are determined by setting the Gibbs free energy of each of these reactions equal to zero, i.e.,

$$\Delta G_j = \Delta G_j^0(T, P) + RT \ln \prod_{i=1}^n a_i^{\nu_{ji}} = 0 \quad (13)$$

These equations are next solved for the variables of interest, i.e., $T, P, a_1, a_2, \dots, a_n$, and analyzed for stable and unstable species. Unstable species are eliminated from further consideration, and the analysis is focused only on the stability boundaries between dominant species.

At a first glance, this thermodynamic analysis seems to be correct. Indeed, eq 13 is nothing but a rigorous representation of the equilibrium conditions. A more careful analysis of the problem, however, reveals that the stability analysis based on eq 13 is both thermodynamically and stoichiometrically inconsistent. The point is that the conditions of chemical equilibrium, eq 13, are not applied properly. Indeed, according to chemical thermodynamics,^{13,14} the chemical equilibrium is completely described by no less than $m = p - \text{rank } \epsilon = n - s$ chemical reactions. Respectively, no less than $m = p - \text{rank } \epsilon = n - s$ of eq 13 should hold *concomitantly* in the entire range of variable changes. Within the conventional stability analysis,

however, eq 13 is *applied separately to individual chemical reactions* while neglecting the remaining reactions. In other words, according to the conventional stability analysis, a complex chemical system is partitioned in a combinatorial manner into one reaction subsystems and the stability relations in each subsystem are analyzed separately. Clearly, this approach is strictly correct only in one chemical reaction system. In the general case of multiple chemical reaction systems, the omission of a substantial part of reactions among species results in incorrect evaluations of the species stability boundaries.

Overall Stability Analysis

Our approach to the evaluation of stability of chemical species may be briefly formulated as follows. We consider an initial state of the system in which the species have a certain value of the partial Gibbs free energy $\bar{G}_i(T, P, a_1, a_2, \dots, a_n)$ ($i = 1, 2, \dots, n$). The species are allowed further to react at constants T and P according to eq 6, thus, arriving at an equilibrium state of the system, i.e., a state of the system in which the partial Gibbs free energies of the species are equal to their equilibrium values $\bar{G}_i^{\text{eq}}(T, P, a_1^{\text{eq}}, a_2^{\text{eq}}, \dots, a_n^{\text{eq}})$ ($i = 1, 2, \dots, n$). Let us define the vectors

$$\bar{G}^{\text{eq}} = (\bar{G}_1^{\text{eq}}, \bar{G}_2^{\text{eq}}, \dots, \bar{G}_n^{\text{eq}})^T \quad (14)$$

$$\Sigma = \bar{G} - \bar{G}^{\text{eq}} = (\bar{G}_1 - \bar{G}_1^{\text{eq}}, \bar{G}_2 - \bar{G}_2^{\text{eq}}, \dots, \bar{G}_n - \bar{G}_n^{\text{eq}})^T \quad (15)$$

If $\Sigma_i = \bar{G}_i - \bar{G}_i^{\text{eq}} > 0$, the species B_i has an excess of Gibbs free energy in the initial state as compared to the equilibrium state and, hence, the Gibbs free energy of the species B_i decreases during the reaction. On the contrary, if $\Sigma_i = \bar{G}_i - \bar{G}_i^{\text{eq}} < 0$, the species B_i has a deficit of Gibbs free energy in the initial state as compared to the equilibrium state and the partial Gibbs free energy of the species B_i increases during the reaction. On the basis of these considerations, the stability/instability criterion of a species B_i in a multiple chemical reaction system is defined as (a) the species B_i is unstable if $\Sigma_i = \bar{G}_i - \bar{G}_i^{\text{eq}} > 0$; (b) the species B_i is stable if $\Sigma_i = \bar{G}_i - \bar{G}_i^{\text{eq}} < 0$; and (c) the species B_i is at equilibrium if $\Sigma_i = \bar{G}_i - \bar{G}_i^{\text{eq}} = 0$

In what follows, the quantities Σ_i ($i = 1, 2, \dots, n$) are referred to as the *overall stabilities*.¹⁵

Evaluation of the Overall Stability of Species

The overall stability vector Σ may be evaluated as follows. First, we require the Gibbs free-energy changes of the reactions ρ at equilibrium to be equal to zero, i.e.,

$$\Delta G^{\text{eq}} = \nu \bar{G}^{\text{eq}} = 0 \quad (16)$$

Subtracting eq 16 from eq 12 gives

$$\Delta G - \Delta G^{\text{eq}} = \Delta G = \nu(\bar{G} - \bar{G}^{\text{eq}})$$

or taking into account eq 15

$$\nu \Sigma = \Delta G \quad (17)$$

Next, the product $\Sigma^T \Sigma$ is minimized subject to the constraints given by eq 17. The procedure has been described in details elsewhere.¹⁶ The result is

$$\Sigma = \nu^T (\nu \nu^T)^{-1} \Delta G \quad (18)$$

Notice that, although the stoichiometric matrix ν is generated arbitrarily, the overall stability vector Σ is unique; in that, Σ is

independent of the choice of ν . A proof of this statement is presented below.

Overall Stability Boundaries and Predominance Diagrams

The overall species stabilities defined and derived above, eq 18, provide a new and thermodynamically consistent approach to the evaluation of the stability boundaries and predominance diagrams in multiple chemical reaction systems. We observe first that the stabilities $\Sigma_i(T, P, a_1, a_2, \dots, a_n)$ ($i = 1, 2, \dots, n$) of *all species* are evaluated analytically. As a result, the stability field for each species is divided into a stable [$\Sigma_i(T, P, a_1, a_2, \dots, a_n) < 0$], equilibrium [$\Sigma_i(T, P, a_1, a_2, \dots, a_n) = 0$], and unstable [$\Sigma_i(T, P, a_1, a_2, \dots, a_n) > 0$] field. We further assume that under given conditions, that is, given values of the variables ($T, P, a_1, a_2, \dots, a_n$), *the species with the lowest overall stability is the dominant species*. This assumption allows us to evaluate analytically the stability boundaries among the dominant species. For instance, if two species B_q and B_s were shown to be dominant, then the stability boundary between them is simply given by $\Sigma_q = \Sigma_s$ or $-\Sigma_q + \Sigma_s = 0$.

Interpretation

The overall stability vector Σ , eq 18, has a remarkable physicochemical meaning. To be able to see it, we consider a special class of reactions, referred to as response reactions (RERs).¹⁷ By definition, a RER is a reaction involving no more than rank $\epsilon + 1 = s + 1$ species. Let $\nu_{\rho i}$ be the stoichiometric coefficients of the species B_i in RER ρ and $\Delta G_\rho(T, P, a_1, a_2, \dots, a_n)$ be the Gibbs free-energy change of the same RER. Let us also agree that the stoichiometric coefficients in a complete set of RERs are chosen as the smallest integers. In this case, as shown in the Appendix, it is convenient to introduce a stoichiometric factor γ_ρ for each RER. Then, the overall stability vector Σ , eq 18, may be partitioned into contributions coming from RERs according to¹²

$$\Sigma_i = \frac{1}{D} \sum_\rho \gamma_\rho^2 \nu_{\rho i} \Delta G_\rho(T, P, a_1, a_2, \dots, a_n) \quad i = 1, 2, \dots, n \quad (19)$$

where

$$D = \frac{1}{m} \sum_\rho \sum_{k=1}^n \gamma_\rho^2 \nu_{\rho k}^2 \quad (20)$$

Notice that D , eq 20, is necessarily a positive quantity. Because the RERs are stoichiometrically unique, the independence of the overall stability vector Σ on the choice of ν is self-evident.

The partition of the overall stability vector into contributions coming from RERs, eq 19, clearly shows the difference between the conventional and the overall stability analysis. Thus, the overall stabilities of the species involve contributions coming from a complete and unique set of reactions among all species, i.e., RERs. Each of these contributions has a simple form, namely, it is a product of a purely stoichiometric term, $\gamma_\rho^2 \nu_{\rho i}$, and a thermodynamic term, $\Delta G_\rho(T, P, a_1, a_2, \dots, a_n)$. In this respect, the overall stabilities of the species may be regarded as a *complete stoichiometric and thermodynamic balance* in the system.

The fundamental difference between the overall and conventional stabilities is best visualized when determining the stability boundaries. As mentioned above, the overall stability boundary

TABLE 1: Standard Gibbs Free Energies of Formation (in kcal/mol) of the Species in the System:
 $K^+_{(aq)} - H^+_{(aq)} - H_4SiO_{4(aq)} - H_2O_{(l)} - Al(OH)_3$
 (Gibbsite) $- Al_2Si_2O_5(OH)_4$ (Kaolinite) $- KAl_3Si_3O_{10}(OH)_2$
 (Muscovite)

	ΔG_{fi}^0
$K^+_{(aq)}$	-67.51
$H_4SiO_{4(aq)}$	-312.60
$H_2O_{(l)}$	-56.69
$H^+_{(aq)}$	0.0
$Al(OH)_3$ (gibbsite)	-276.17
$Al_2Si_2O_5(OH)_4$ (kaolinite)	-905.61
$KAl_3Si_3O_{10}(OH)_2$ (muscovite)	-1336.30

between two species, say, B_q and B_s , is given by $-\Sigma_q + \Sigma_s = 0$ or, in terms of RERs, eq 19

$$\sum_\rho \gamma_\rho^2 (\nu_{\rho s} - \nu_{\rho q}) \Delta G_\rho(T, P, a_1, a_2, \dots, a_n) = 0 \quad (21)$$

As can be seen, the overall stability boundary between two species is a sum of contributions from all of the RERs involving these two species concomitantly. On the contrary, the conventional stability boundary is determined solely based on a single RER, eq 13. It is in this sense that the conventional stability analysis is stoichiometrically and thermodynamically inconsistent.

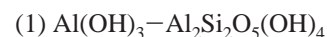
Finally, we notice that the partition of the overall stabilities into contributions coming from RERs allows us to determine the dominant RERs. Indeed, according to eq 19, the dominant contributions are expected from the RERs for which the product $\gamma_\rho^2 \Delta G_\rho(T, P, a_1, a_2, \dots, a_n)$ is the highest.

Examples

The theoretical developments presented above are next illustrated with the help of two simple examples. One of them describes the chemical equilibrium in a heterogeneous system involving minerals. The conventional stability boundaries in such systems are referred to as *stability diagrams*.⁸ The second example discusses the stability relations in an electrochemical system. Usually the stability boundaries in such systems are known as *Pourbaix diagrams*.²

Stability Diagram. Consider the stability relations in a heterogeneous system comprising three pure solid phases, namely, $Al(OH)_3$ (gibbsite), $Al_2Si_2O_5(OH)_4$ (kaolinite), and $KAl_3Si_3O_{10}(OH)_2$ (muscovite) in equilibrium with an ideal aqueous phase containing dissolved species $H_4SiO_{4(aq)}$, $K^+_{(aq)}$, and $H^+_{(aq)}$. Observe that to reduce the number of variables, $Al^{3+}_{(aq)}$ has been omitted.⁸ The Gibbs free energies of formation of the species comprising this system were taken from ref 8 and are presented in Table 1.

Conventional Stability Diagram. The goal of the conventional stability analysis in this system is to determine the boundaries that limit the stability fields of the three minerals $Al(OH)_3$ (gibbsite), $Al_2Si_2O_5(OH)_4$ (kaolinite), and $KAl_3Si_3O_{10}(OH)_2$ (muscovite) as a function of $a_{H_4SiO_4}$ and a_{K^+}/a_{H^+} at standard T and P . In doing this, the chemical reactions that involve the three possible pairs of minerals are first generated. These reactions, along with their standard Gibbs free-energy changes (in kcal/mol), are

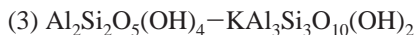


$$\rho_1 = 2H_4SiO_4 - 5H_2O + 2Al(OH)_3 - Al_2Si_2O_5(OH)_4 = 0$$

$$\Delta G_1^0 = 11.52$$



$$\rho_2 = \text{K}^+ + 3\text{H}_4\text{SiO}_4 - 9\text{H}_2\text{O} - \text{H}^+ + 3\text{Al(OH)}_3 - \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 = 0 \quad \Delta G_2^0 = 12.69$$



$$\rho_3 = 2\text{K}^+ - 3\text{H}_2\text{O} - 2\text{H}^+ + 3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 - 2\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 = 0 \quad \Delta G_3^0 = -9.18$$

Because the activity of the solid phases and water are equal to one, the Gibbs free-energy changes of the reactions are

$$\Delta G_1 = \Delta G_1^0 + 2RT \ln a_{\text{H}_4\text{SiO}_4} \quad (22)$$

$$\Delta G_2 = \Delta G_2^0 + 3RT \ln a_{\text{H}_4\text{SiO}_4} + RT \ln \frac{a_{\text{K}^+}}{a_{\text{H}^+}} \quad (23)$$

$$\Delta G_3 = \Delta G_3^0 + 2RT \ln \frac{a_{\text{K}^+}}{a_{\text{H}^+}} \quad (24)$$

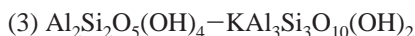
The conventional stability boundaries between Al(OH)_3 , $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, and $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ are obtained by setting separately ΔG_1 , ΔG_2 , and ΔG_3 equal to zero. This gives three straight lines in logarithmic coordinates $\ln a_{\text{H}_4\text{SiO}_4}$ and $\ln(a_{\text{K}^+}/a_{\text{H}^+})$



$$\Delta G_1 = 0 \quad \ln a_{\text{H}_4\text{SiO}_4} = -\frac{\Delta G_1^0}{2RT} \quad (25)$$



$$\Delta G_2 = 0 \quad \ln a_{\text{H}_4\text{SiO}_4} + \ln \frac{a_{\text{K}^+}}{a_{\text{H}^+}} = -\frac{\Delta G_2^0}{RT} \quad (26)$$



$$\Delta G_3 = 0 \quad \ln \frac{a_{\text{K}^+}}{a_{\text{H}^+}} = -\frac{\Delta G_3^0}{RT} \quad (27)$$

These straight lines represent the conventional stability boundaries of the three minerals and are graphically depicted in Figure 1.

It should be noticed that the number of linearly independent chemical reactions in this system is equal to two, and hence, two chemical reactions are needed to describe the equilibrium condition in the system. In the meantime, the conventional stability analysis of the system $\{\text{K}^+, \text{H}_4\text{SiO}_4, \text{H}_2\text{O}, \text{H}^+, \text{Al(OH)}_3, \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4, \text{and KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2\}$ has been performed based on the equilibrium condition of three separate one-reaction subsystems, namely, (1) $\{\text{K}^+, \text{H}_4\text{SiO}_4, \text{H}_2\text{O}, \text{H}^+, \text{Al(OH)}_3, \text{and Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\}$, (2) $\{\text{K}^+, \text{H}_4\text{SiO}_4, \text{H}_2\text{O}, \text{H}^+, \text{Al(OH)}_3, \text{and KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2\}$ and (3) $\{\text{K}^+, \text{H}_4\text{SiO}_4, \text{H}_2\text{O}, \text{H}^+, \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4, \text{and KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2\}$. Only in the particular case when the stability boundaries intersect, the Gibbs free-energy changes of all three reactions are concomitantly equal to zero.

Overall Stability Diagram. Let us now analyze the stability boundaries of the species employing the overall stability approach. Our starting point is a set of linearly independent reactions. These can be generated using a standard procedure.¹³

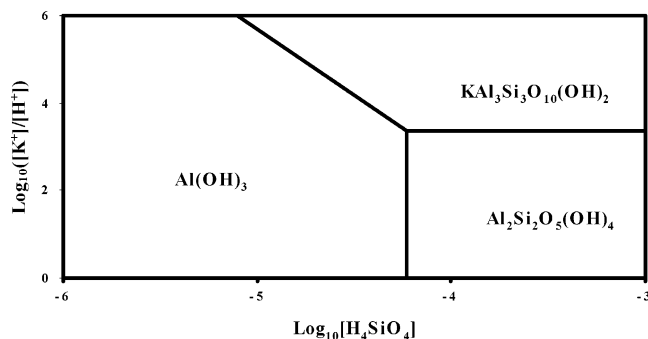


Figure 1. Conventional Stability diagram for the system: $\text{K}^+_{(\text{aq})}-\text{H}^+_{(\text{aq})}-\text{H}_4\text{SiO}_{4(\text{aq})}-\text{H}_2\text{O}_{(\text{l})}-\text{Al(OH)}_3$ (gibbsite)- $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolinite)- $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ (muscovite).

In particular, an appropriate choice of a set of linearly independent reactions is

$$\rho_1 = 2\text{H}_4\text{SiO}_4 - 5\text{H}_2\text{O} + 2\text{Al(OH)}_3 - \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 = 0$$

$$\Delta G_1 = \Delta G_1^0 + 2RT \ln a_{\text{H}_4\text{SiO}_4}$$

$$\rho_2 = \text{K}^+ + 3\text{H}_4\text{SiO}_4 - 9\text{H}_2\text{O} - \text{H}^+ + 3\text{Al(OH)}_3 - \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 = 0$$

$$\Delta G_2 = \Delta G_2^0 + 3RT \ln a_{\text{H}_4\text{SiO}_4} + RT \ln \frac{a_{\text{K}^+}}{a_{\text{H}^+}}$$

The respective stoichiometric matrix ν and Gibbs free-energy change vector ΔG are

$$\nu = \begin{bmatrix} 0 & 2 & -5 & 0 & 2 & -1 & 0 \\ 1 & 3 & -9 & -1 & 3 & 0 & -1 \end{bmatrix} \begin{matrix} \rho_1 \\ \rho_2 \end{matrix}$$

$$\Delta G = \begin{pmatrix} \Delta G_1 \\ \Delta G_2 \end{pmatrix} = \begin{pmatrix} \Delta G_1^0 + 2RT \ln a_{\text{H}_4\text{SiO}_4} \\ \Delta G_2^0 + 3RT \ln a_{\text{H}_4\text{SiO}_4} + RT \ln \frac{a_{\text{K}^+}}{a_{\text{H}^+}} \end{pmatrix}$$

Substituting these relations into eq 18 and performing the respective matrix operations gives

$$\Sigma_{\text{K}^+} = \frac{1}{219}[-57\Delta G_1 + 34\Delta G_2] = \frac{1}{219} \left[-57\Delta G_1^0 + 34\Delta G_2^0 - 12RT \ln a_{\text{H}_4\text{SiO}_4} + 34RT \ln \frac{a_{\text{K}^+}}{a_{\text{H}^+}} \right] \quad (28)$$

$$\Sigma_{\text{H}_4\text{SiO}_4} = \frac{1}{73}[11\Delta G_1 - 4\Delta G_2] = \frac{1}{73} \left[11\Delta G_1^0 - 4\Delta G_2^0 + 10RT \ln a_{\text{H}_4\text{SiO}_4} - 4RT \ln \frac{a_{\text{K}^+}}{a_{\text{H}^+}} \right] \quad (29)$$

$$\Sigma_{\text{H}_2\text{O}} = \frac{1}{73}[\Delta G_1 - 7\Delta G_2] = \frac{1}{73} \left[\Delta G_1^0 - 7\Delta G_2^0 - 19RT \ln a_{\text{H}_4\text{SiO}_4} - 7RT \ln \frac{a_{\text{K}^+}}{a_{\text{H}^+}} \right] \quad (30)$$

$$\Sigma_{H^+} = \frac{1}{219}[57\Delta G_1 - 34\Delta G_2] = \frac{1}{219}\left[57\Delta G_1^0 - 34\Delta G_2^0 + 12RT \ln a_{H_4SiO_4} - 34RT \ln \frac{a_{K^+}}{a_{H^+}}\right] \quad (31)$$

$$\Sigma_{Al(OH)_3} = \frac{1}{73}[11\Delta G_1 - 4\Delta G_2] = \frac{1}{73}\left[11\Delta G_1^0 - 4\Delta G_2^0 + 10RT \ln a_{H_4SiO_4} - 4RT \ln \frac{a_{K^+}}{a_{H^+}}\right] \quad (32)$$

$$\Sigma_{Al_2Si_2O_5(OH)_4} = \frac{1}{73}[-34\Delta G_1 + 19\Delta G_2] = \frac{1}{73}\left[-34\Delta G_1^0 + 19\Delta G_2^0 - 11RT \ln a_{H_4SiO_4} + 19RT \ln \frac{a_{K^+}}{a_{H^+}}\right] \quad (33)$$

$$\Sigma_{KAl_3Si_3O_{10}(OH)_2} = \frac{1}{219}[57\Delta G_1 - 34\Delta G_2] = \frac{1}{219}\left[57\Delta G_1^0 - 34\Delta G_2^0 + 12RT \ln a_{H_4SiO_4} - 34RT \ln \frac{a_{K^+}}{a_{H^+}}\right] \quad (34)$$

As can be seen, the overall stabilities of all species are explicit functions of the variables that govern the position of chemical equilibrium, i.e., $\ln a_{H_4SiO_4}$ and $\ln(a_{K^+}/a_{H^+})$, and can be easily evaluated numerically. For instance, at $a_{H_4SiO_4} = 10^{-5}$, $a_{K^+}/a_{H^+} = 10^3$, and $T = 298$ K, the overall stabilities of the species (in kcal/mol) are $\Sigma_{K^+} = -0.02$, $\Sigma_{H_4SiO_4} = -0.12$, $\Sigma_{H_2O} = -0.32$, $\Sigma_{H^+} = 0.02$, $\Sigma_{Al(OH)_3} = -0.12$, $\Sigma_{Al_2Si_2O_5(OH)_4} = 0.03$, and $\Sigma_{KAl_3Si_3O_{10}(OH)_2} = 0.02$. Hence, under these conditions, $K^+_{(aq)}$, $H_4SiO_{4(aq)}$, and $Al(OH)_3$ are stable, while $H_2O_{(l)}$, $H^+_{(aq)}$, $Al_2Si_2O_5(OH)_4$, and $KAl_3Si_3O_{10}(OH)_2$ are unstable. The stability boundaries of the solid phases are obtained by equalizing their overall stabilities

$$\begin{aligned} (1) & Al(OH)_3 - Al_2Si_2O_5(OH)_4 \\ & -\Sigma_{Al(OH)_3} + \Sigma_{Al_2Si_2O_5(OH)_4} = 0 \\ & -45\Delta G_1 + 23\Delta G_2 = 0 \\ & 21 \ln a_{H_4SiO_4} - 23 \ln \frac{a_{K^+}}{a_{H^+}} = -\frac{(45\Delta G_1^0 - 23\Delta G_2^0)}{RT} \\ (2) & Al(OH)_3 - KAl_3Si_3O_{10}(OH)_2 \\ & -\Sigma_{Al(OH)_3} + \Sigma_{KAl_3Si_3O_{10}(OH)_2} = 0 \\ & 12\Delta G_1 - 11\Delta G_2 = 0 \\ & 9 \ln a_{H_4SiO_4} + 11 \ln \frac{a_{K^+}}{a_{H^+}} = \frac{(12\Delta G_1^0 - 11\Delta G_2^0)}{RT} \\ (3) & Al_2Si_2O_5(OH)_4 - KAl_3Si_3O_{10}(OH)_2 \\ & -\Sigma_{Al_2Si_2O_5(OH)_4} + \Sigma_{KAl_3Si_3O_{10}(OH)_2} = 0 \\ & 159\Delta G_1 - 91\Delta G_2 = 0 \\ & 45 \ln a_{H_4SiO_4} - 91 \ln \frac{a_{K^+}}{a_{H^+}} = -\frac{(159\Delta G_1^0 - 91\Delta G_2^0)}{RT} \end{aligned}$$

These overall stability boundaries are graphically depicted in Figure 2. When Figures 1 and 2 are compared, it is seen that the overall stability field of $Al(OH)_3$ is substantially reduced as compared to its conventional stability field.

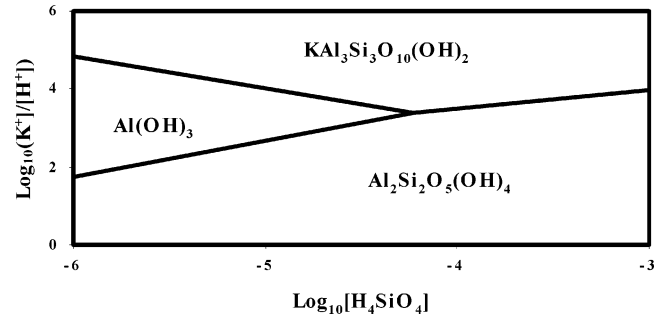


Figure 2. Overall Stability diagram for the system: $K^+_{(aq)} - H^+_{(aq)} - H_4SiO_{4(aq)} - H_2O_{(l)} - Al(OH)_3$ (gibbsite) $- Al_2Si_2O_5(OH)_4$ (kaolinite) $- KAl_3Si_3O_{10}(OH)_2$ (muscovite).

TABLE 2: Stoichiometric Factors and Standard Gibbs Free Changes (in kcal/mol) of the RERs for the System:
 $K^+_{(aq)} - H^+_{(aq)} - H_4SiO_{4(aq)} - H_2O_{(l)} - Al(OH)_3$ (Gibbsite) $- Al_2Si_2O_5(OH)_4$ (Kaolinite) $- KAl_3Si_3O_{10}(OH)_2$ (Muscovite)

RER	γ_j^2	ΔG_j^0
$\rho_1 = 2H_4SiO_4 - 5H_2O + 2Al(OH)_3 - Al_2Si_2O_5(OH)_4 = 0$	3	11.52
$\rho_2 = K^+ + 3H_3SiO_4 - 9H_2O - H^+ + 3Al(OH)_3 - KAl_3Si_3O_{10}(OH)_2 = 0$	1	12.69
$\rho_3 = 2K^+ - 3H_2O - 2H^+ + 3Al_2Si_2O_5(OH)_4 - 2KAl_3Si_3O_{10}(OH)_2 = 0$	2	-9.18
$\rho_4 = -5K^+ + 3H_4SiO_4 + 5H^+ + 3Al(OH)_3 - 9Al_2Si_2O_5(OH)_4 + 5KAl_3Si_3O_{10}(OH)_2 = 0$	1	40.23

A deeper insight into the thermodynamic and stoichiometric aspects of the overall stability relations in this system, as well as the interrelationship between the conventional and overall stability analysis, may be obtained by partitioning the overall stabilities of the species into contributions coming from RERs, eq 19. A complete list of RERs and their stoichiometric factors are generated in the Appendix and presented in Table 2. An inspection of Table 2 reveals that the conventional stability analysis involves only three RERs from a total of four, namely, the first three RERs, while the overall stability analysis involves all four RERs. Thus, according to eq 19, the overall species stabilities may be partitioned into contributions coming for RERs as

$$\Sigma_{K^+} = \frac{1}{219}(\Delta G_2 + 4\Delta G_3 - 5\Delta G_4) \quad (35)$$

$$\Sigma_{H_4SiO_4} = \frac{1}{219}(6\Delta G_1 + 3\Delta G_2 + 3\Delta G_4) \quad (36)$$

$$\Sigma_{H_2O} = \frac{1}{219}(-15\Delta G_1 - 9\Delta G_2 - 6\Delta G_4) \quad (37)$$

$$\Sigma_{H^+} = \frac{1}{219}(-\Delta G_2 - 4\Delta G_3 + 5\Delta G_4) \quad (38)$$

$$\Sigma_{Al(OH)_3} = \frac{1}{219}(6\Delta G_1 + 3\Delta G_2 + 3\Delta G_4) \quad (39)$$

$$\Sigma_{Al_2Si_2O_5(OH)_4} = \frac{1}{219}(-3\Delta G_1 + 6\Delta G_3 - 9\Delta G_4) \quad (40)$$

$$\Sigma_{KAl_3Si_3O_{10}(OH)_2} = \frac{1}{219}(-\Delta G_2 - 4\Delta G_3 + 5\Delta G_4) \quad (41)$$

Equations 35–41 are equivalent to eqs 28–34. This can be easily proven by observing that the RERs are linearly dependent, e.g., $\rho_3 = -3\rho_1 + 2\rho_2$ and $\rho_4 = 9\rho_1 - 5\rho_2$ and, consequently, $\Delta G_3 = -3\Delta G_1 + 2\Delta G_2$ and $\Delta G_4 = 9\Delta G_1 - 5\Delta G_2$. Now, the overall stability boundaries between the minerals in terms of RER according to eq 21 are

$$\begin{aligned}
 (1) & \text{Al(OH)}_3 - \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \\
 & -\Sigma_{\text{Al(OH)}_3} + \Sigma_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4} = 0 \\
 3\Delta G_1 + \Delta G_2 - 2\Delta G_3 + 4\Delta G_4 &= 0 \quad (42)
 \end{aligned}$$

$$\begin{aligned}
 (2) & \text{Al(OH)}_3 - \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 \\
 & -\Sigma_{\text{Al(OH)}_3} + \Sigma_{\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2} = 0 \\
 3\Delta G_1 + 2\Delta G_2 + 2\Delta G_3 - \Delta G_4 &= 0 \quad (43)
 \end{aligned}$$

$$\begin{aligned}
 (3) & \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 - \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 \\
 & -\Sigma_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4} + \Sigma_{\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2} = 0 \\
 -3\Delta G_1 + \Delta G_2 + 10\Delta G_3 - 14\Delta G_4 &= 0 \quad (44)
 \end{aligned}$$

These overall stability boundaries should be compared with the conventional stability boundaries, eqs 25–27. The difference between the two approaches is self-evident.

Pourbaix Diagram. As a second example, we consider the stability relations in an ideal aqueous solution comprising six species, namely, $e^-_{(\text{aq})}$ (electron), $\text{H}^+_{(\text{aq})}$, $\text{H}_2\text{O}_{(\text{l})}$, $\text{Fe}^{2+}_{(\text{aq})}$, $\text{Fe(OH)}_{2(\text{s})}$, and $\text{Fe}_{(\text{s})}$. The natural variables that govern the stability relations in aqueous systems involving electrons are the pH and potential E (on hydrogen scale) defined as

$$\begin{aligned}
 \text{pH} &= -\log_{10} a_{\text{H}^+} \\
 E &= -\frac{2.3RT}{F} \log_{10} a_{e^-}
 \end{aligned}$$

Here, F is the Faraday constant. For simplicity, in what follows, we assume that the activity of water and Fe^{2+} are equal to one, while the solid phases are assumed to be pure phases. The standard Gibbs free energies of formation of the species¹⁸ are presented in Table 3.

Conventional Pourbaix Diagram. The conventional stability analysis in this system focuses only on the Fe-containing species, i.e., $\text{Fe}^{2+}_{(\text{aq})}$, $\text{Fe(OH)}_{2(\text{s})}$, and $\text{Fe}_{(\text{s})}$. The first step in the construction of the Pourbaix diagram is the generation of a set of chemical reactions involving all pairs of the Fe-containing species. These are

$$\begin{aligned}
 \rho_1 &= -2\text{H}^+ + 2\text{H}_2\text{O} + \text{Fe}^{2+} - \text{Fe(OH)}_2 = 0 \\
 \Delta G_1^0 &= -18.85 \text{ kcal/mol} \\
 \rho_2 &= 2e^- + \text{Fe}^{2+} - \text{Fe} = 0 \quad \Delta G_2^0 = -21.88 \text{ kcal/mol} \\
 \rho_3 &= 2e^- + 2\text{H}^+ - 2\text{H}_2\text{O} + \text{Fe(OH)}_2 - \text{Fe} = 0 \\
 \Delta G_3^0 &= -3.03 \text{ kcal/mol}
 \end{aligned}$$

Next, the Gibbs free-energy changes of these reactions as explicit functions of E and pH are evaluated

$$\begin{aligned}
 \Delta G_1 &= \Delta G_1^0 + 2(2.3RT\text{pH}) \\
 \Delta G_2 &= \Delta G_2^0 - 2FE \\
 \Delta G_3 &= \Delta G_3^0 - 2FE - 2(2.3RT\text{pH})
 \end{aligned}$$

The stability boundaries of the Fe-containing species are next

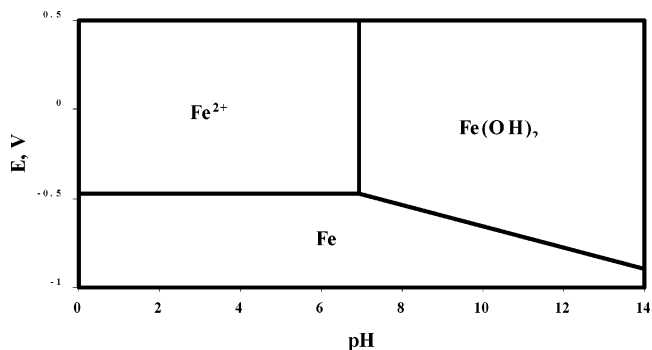


Figure 3. Conventional Pourbaix diagram for the system: $e^-_{(\text{aq})}$ – $\text{H}^+_{(\text{aq})}$ – $\text{H}_2\text{O}_{(\text{l})}$ – $\text{Fe}^{2+}_{(\text{aq})}$ – $\text{Fe(OH)}_{2(\text{s})}$ – $\text{Fe}_{(\text{s})}$.

TABLE 3. Standard Gibbs Free Energies of Formation (in kcal/mol) of the Species in the System: $e^-_{(\text{aq})}$ – $\text{H}^+_{(\text{aq})}$ – $\text{H}_2\text{O}_{(\text{l})}$ – $\text{Fe}^{2+}_{(\text{aq})}$ – $\text{Fe(OH)}_{2(\text{s})}$ – $\text{Fe}_{(\text{s})}$

	$\Delta G_{f,i}^0$		$\Delta G_{f,i}^0$
$e^-_{(\text{aq})}$	0.0	$\text{Fe}^{2+}_{(\text{aq})}$	–21.88
$\text{H}^+_{(\text{aq})}$	0.0	$\text{Fe(OH)}_{2(\text{s})}$	–116.39
$\text{H}_2\text{O}_{(\text{l})}$	–56.68	$\text{Fe}_{(\text{s})}$	0.0

obtained by setting ΔG_1 , ΔG_2 , and ΔG_3 equal to zero, thus resulting in three straight lines in the coordinates E – pH

$$(1) \text{Fe}^{2+} - \text{Fe(OH)}_2$$

$$\Delta G_1 = 0 \quad \text{pH} = -\frac{\Delta G_1^0}{2(2.3RT)} \quad (45)$$

$$(2) \text{Fe}^{2+} - \text{Fe}$$

$$\Delta G_2 = 0 \quad E = -\frac{\Delta G_2^0}{2F} \quad (46)$$

$$(2) \text{Fe(OH)}_2 - \text{Fe}$$

$$\Delta G_3 = 0 \quad E + \frac{2.3RT}{F}\text{pH} = \frac{\Delta G_3^0}{2F} \quad (47)$$

The conventional Pourbaix diagram is shown in Figure 3.

We notice that from a thermodynamic point of view, the chemical equilibrium in this system may be described by a set of two linearly independent reactions. The conventional stability analysis, however, is based on the equilibrium conditions of three separate reactions that correspond to three one-reactions subsystems, namely, (1) $\{e^-, \text{H}^+, \text{H}_2\text{O}, \text{Fe}^{2+}, \text{and Fe(OH)}_2\}$, (2) $\{e^-, \text{H}^+, \text{H}_2\text{O}, \text{Fe}^{2+}, \text{and Fe}\}$, and (3) $\{e^-, \text{H}^+, \text{H}_2\text{O}, \text{Fe}, \text{and Fe(OH)}_2\}$. Only in the particular case when the stability boundaries of all three Fe species intersect, the Gibbs free-energy changes of all three reactions are concomitantly equal to zero; i.e., only at this point, the equilibrium is described correctly.

Overall Pourbaix Diagram. According to the overall stability analysis, the starting point in the evaluation of the stability boundaries is an arbitrary set of linearly independent reactions. We select these reactions as

$$\begin{aligned}
 \rho_1 &= -2\text{H}^+ + 2\text{H}_2\text{O} + \text{Fe}^{2+} - \text{Fe(OH)}_2 = 0 \\
 \Delta G_1^0 &= -18.85 \text{ kcal/mol}
 \end{aligned}$$

$$\rho_2 = 2e^- + \text{Fe}^{2+} - \text{Fe} = 0 \quad \Delta G_2^0 = -21.88 \text{ kcal/mol}$$

This gives the following stoichiometric matrix and Gibbs free-

energy changes vector

$$\mathbf{v} = \begin{bmatrix} 0 & -2 & 2 & 1 & -1 & 0 \\ 2 & 0 & 0 & 1 & 0 & -1 \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \end{bmatrix}$$

$$\Delta \mathbf{G} = \begin{pmatrix} \Delta G_1 \\ \Delta G_2 \end{pmatrix} = \begin{pmatrix} \Delta G_1^0 + 2(2.3RT\text{pH}) \\ \Delta G_2^0 - 2FE \end{pmatrix}$$

Substituting these relations into eq 18 and performing the respective matrix operations gives

$$\Sigma_{e^-} = -\frac{2}{59}(\Delta G_1 - 10\Delta G_2) = -\frac{2}{59}(\Delta G_1^0 - 10\Delta G_2^0 + 20FE + 2(2.3RT\text{pH})) \quad (48)$$

$$\Sigma_{H^+} = -\frac{2}{59}(6\Delta G_1 - \Delta G_2) = -\frac{2}{59}(6\Delta G_1^0 - \Delta G_2^0 + 2FE + 12(2.3RT\text{pH})) \quad (49)$$

$$\Sigma_{H_2O} = \frac{2}{59}(6\Delta G_1 - \Delta G_2) = \frac{2}{59}(6\Delta G_1^0 - \Delta G_2^0 + 2FE + 12(2.3RT\text{pH})) \quad (50)$$

$$\Sigma_{Fe^{2+}} = \frac{1}{59}(5\Delta G_1 + 9\Delta G_2) = \frac{1}{59}(5\Delta G_1^0 + 9\Delta G_2^0 - 18FE + 10(2.3RT\text{pH})) \quad (51)$$

$$\Sigma_{Fe(OH)_2} = \frac{1}{59}(-6\Delta G_1 + \Delta G_2) = \frac{1}{59}(-6\Delta G_1^0 + \Delta G_2^0 - 2FE - 12(2.3RT\text{pH})) \quad (52)$$

$$\Sigma_{Fe} = \frac{1}{59}(\Delta G_1 - 10\Delta G_2) = \frac{1}{59}(\Delta G_1^0 - 10\Delta G_2^0 + 20FE + 2(2.3RT\text{pH})) \quad (53)$$

Again, the overall stabilities of all species are analytical functions of the variables that govern the position of chemical equilibrium in the system, i.e., E and pH . For instance, at $E = 0$ and $\text{pH} = 0$, the overall stabilities of the species (in kcal/mol) are $\Sigma_{e^-} = -6.88$, $\Sigma_{H^+} = 3.09$, $\Sigma_{H_2O} = -3.09$, $\Sigma_{Fe^{2+}} = -4.94$, $\Sigma_{Fe(OH)_3} = 1.55$, and $\Sigma_{Fe} = 3.89$. Hence, for these particular values of E and pH , the only stable species in the system are e^- , H_2O , and Fe^{2+} . Alternatively, the overall stability relations may be presented graphically as boundaries between the most abundant Fe species in the coordinates $E - \text{pH}$. These boundaries may be determined by equalizing the overall species stabilities

$$\begin{aligned} (1) \quad & Fe^{2+} - Fe(OH)_2 \\ & -\Sigma_{Fe^{2+}} + \Sigma_{Fe(OH)_2} = 0 \\ & 11\Delta G_1 + 8\Delta G_2 = 0 \\ & 16E - 22\frac{2.3RT}{F}\text{pH} = -\frac{(11\Delta G_1^0 + 8\Delta G_2^0)}{F} \quad (54) \end{aligned}$$

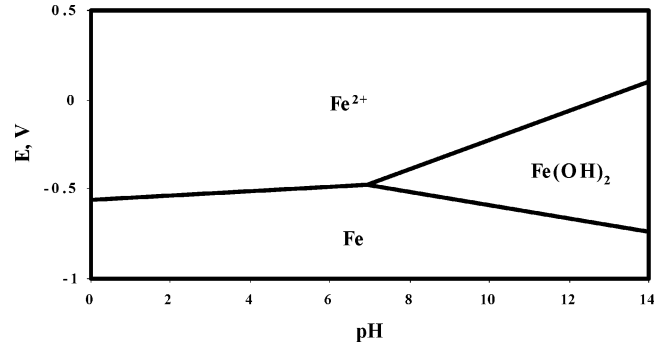


Figure 4. Overall Pourbaix diagram for the system: $e^-_{(aq)} - H^+_{(aq)} - H_2O_{(l)} - Fe^{2+}_{(aq)} - Fe(OH)_{2(s)} - Fe_{(s)}$.

TABLE 4: Stoichiometric Factors and Standard Gibbs Free Changes (in kcal/mol) of the RERs for the System: $e^-_{(aq)} - H^+_{(aq)} - H_2O_{(l)} - Fe^{2+}_{(aq)} - Fe(OH)_{2(s)} - Fe_{(s)}$

RER	γ_j^2	ΔG_i^0
$\rho_1 = -2H^+ + 2H_2O + Fe^{2+} - Fe(OH)_2 = 0$	5	-18.85
$\rho_2 = 2e^- + Fe^{2+} - Fe = 0$	9	-21.88
$\rho_3 = 2e^- + 2H^+ - 2H_2O + Fe(OH)_2 - Fe = 0$	1	-3.03

$$\begin{aligned} (2) \quad & Fe^{2+} - Fe \\ & -\Sigma_{Fe^{2+}} + \Sigma_{Fe} = 0 \\ & 4\Delta G_1 + 19\Delta G_2 = 0 \\ & 38E - 8\frac{2.3RT}{F}\text{pH} = -\frac{(4\Delta G_1^0 + 19\Delta G_2^0)}{F} \quad (55) \end{aligned}$$

$$\begin{aligned} (3) \quad & Fe(OH)_2 - Fe \\ & -\Sigma_{Fe(OH)_2} + \Sigma_{Fe} = 0 \\ & 7\Delta G_1 - 11\Delta G_2 = 0 \\ & 22E + 14\frac{2.3RT}{F}\text{pH} = -\frac{(7\Delta G_1^0 - 11\Delta G_2^0)}{F} \quad (56) \end{aligned}$$

The resulting overall Pourbaix diagram is shown in Figure 4.

A comparison between the conventional and overall Pourbaix diagrams shows that the overall stability field of $Fe(OH)_{2(s)}$ is significantly reduced. To understand this difference, let us partition the overall stabilities of the Fe species into contributions associated with RERs. A complete list of stoichiometrically distinct RERs in this system is presented in Table 4. It is seen that the number of stoichiometrically distinct RERs is equal to the number of reactions that is used in the conventional stability analysis. Yet, the conventional and overall stability relations essentially differ. To visualize this difference, consider the overall stability boundaries of the species in terms of RERs. From Table 4 and eq 21, we obtain

$$\begin{aligned} (1) \quad & Fe^{2+} - Fe(OH)_2 \\ & -\Sigma_{Fe^{2+}} + \Sigma_{Fe(OH)_2} = 0 \\ & 10\Delta G_1 + 9\Delta G_2 - \Delta G_3 = 0 \quad (57) \end{aligned}$$

$$\begin{aligned} (2) \quad & Fe^{2+} - Fe \\ & -\Sigma_{Fe^{2+}} + \Sigma_{Fe} = 0 \\ & 5\Delta G_1 + 18\Delta G_2 + \Delta G_3 = 0 \quad (58) \end{aligned}$$



$$-\Sigma_{\text{Fe(OH)}_3} + \Sigma_{\text{Fe}} = 0$$

$$5\Delta G_1 - 9\Delta G_2 - 2\Delta G_3 = 0 \quad (59)$$

Because $\rho_3 = -\rho_1 + \rho_2$ and $\Delta G_3 = -\Delta G_1 + \Delta G_2$, it is readily seen that eqs 57–59 are equivalent to eqs 54–56. The differences between the conventional and overall Pourbaix diagram may be seen by comparing eqs 45–47 with eqs 57–59.

Discussion and Concluding Remarks

It is long and well-known that the evaluation of different types of stabilities among chemical species may be performed only employing concomitantly thermodynamic and stoichiometric considerations. That is, quantitative thermodynamic data are meant to answer the question “how stable?”, while stoichiometric relations are meant to answer the question “stable with respect to what?”. Traditionally, the stability relations in multiple chemical reaction systems are studied employing graphical methods by evaluating and plotting the stability boundaries of chemical species. The stability boundaries are conventionally determined from the equilibrium conditions of single reactions. In fact, this approach is tantamount to a combinatorial partition of a multiple chemical reaction system into several one-reaction subsystems. Each of these one-reaction subsystems is studied separately; i.e., it is tacitly assumed that the overall equilibrium conditions in a multiple chemical reaction system may be substituted with a set of equilibrium conditions of individual one-reaction subsystems. Obviously, this approach violates the equilibrium conditions in a multiple chemical reaction system, in that, at equilibrium, the Gibbs free-energy change of any conceivable reaction should be equal to zero.

In this work, we addressed the problem of stability of chemical species in multiple chemical reaction systems from a different point of view. Our approach is based on a quantity that is directly related to the stability of chemical species. This function, referred to here as the overall stability, is just the change in the partial Gibbs free energy of the species when the system is moving from a given initial state to an equilibrium state. The overall stabilities of species are evaluated by combining the usual thermodynamic and stoichiometric formalism with the least-squares method. Thus, the overall stability approach ensures rigorous equilibrium conditions of the whole system at any point in the variable space. It is further shown that the overall stabilities have a remarkable physicochemical meaning. More specifically, the overall stabilities may be partitioned into a sum of contributions associated with a unique set of RERs. In this respect, the overall stability of the species may be considered as an exact, complete, and unique thermodynamic and stoichiometric balance in the system.

Appendix

From chemical reaction thermodynamics, it is known that the absolute values of stoichiometric coefficients in chemical reactions are not important; i.e., what really counts is their ratio. Thus, provided γ is different from a zero constant, the reaction

$$\rho = \nu_1 B_1 + \nu_2 B_2 + \dots + \nu_n B_n = 0$$

is equivalent to

$$\gamma\rho = \gamma\nu_1 B_1 + \gamma\nu_2 B_2 + \dots + \gamma\nu_n B_n = 0$$

Normally, the stoichiometric coefficients in chemical reactions are selected as the smallest integers. When describing a multiple chemical reaction system in terms of RERs, however, the stoichiometric coefficients of individual RERs cannot be separately selected as equal to the smallest integers. To prove this statement, let us present a complete set of RERs, $\rho'(B_{i_1}, B_{i_2}, \dots, B_{i_s}, B_{i_{s+1}})$, in the form

$$\rho'(B_{i_1}, B_{i_2}, \dots, B_{i_s}, B_{i_{s+1}}) = \gamma_\rho \rho(B_{i_1}, B_{i_2}, \dots, B_{i_s}, B_{i_{s+1}}) \quad (A1)$$

where $\rho(B_{i_1}, B_{i_2}, \dots, B_{i_s}, B_{i_{s+1}})$ is a RER in which the stoichiometric coefficients are the smallest integers and γ_ρ is a constant. Equation A1 implies that the stoichiometric coefficients of the species B_i in $\rho'(B_{i_1}, B_{i_2}, \dots, B_{i_s}, B_{i_{s+1}})$ and $\rho(B_{i_1}, B_{i_2}, \dots, B_{i_s}, B_{i_{s+1}})$ are interrelated via

$$\nu_{\rho'i} = \gamma_\rho \nu_{\rho i} \quad (A2)$$

Similarly, if $\Delta G_{\rho'}$ is the Gibbs free-energy change of $\rho'(B_{i_1}, B_{i_2}, \dots, B_{i_s}, B_{i_{s+1}})$ and ΔG_ρ is the Gibbs free-energy change of $\rho(B_{i_1}, B_{i_2}, \dots, B_{i_s}, B_{i_{s+1}})$, we have

$$\Delta G_{\rho'} = \gamma_\rho \Delta G_\rho \quad (A3)$$

If the overall stabilities of the species are expressed in terms of $\rho'(B_{i_1}, B_{i_2}, \dots, B_{i_s}, B_{i_{s+1}})$, we have

$$\Sigma_i = \frac{\sum_{\rho'} \nu_{\rho'i} \Delta G_{\rho'}(T, P, a_1, a_2, \dots, a_n)}{-\sum_{\rho'} \sum_{k=1}^n \nu_{\rho'k}^2} \quad i = 1, 2, \dots, n \quad (A4)$$

Substituting eqs A1 and A3 into A4 gives eq 19. As can be seen from eq 19, the constants γ_ρ cannot be canceled and, consequently, are a fundamental stoichiometric characteristic of a multiple chemical reaction system. It is appropriate to call γ_ρ a *stoichiometric factor of a RER*. It should be stressed that the absolute values of γ_ρ are not important. It is the ratio of various γ_ρ that counts. In this respect, it is natural to select the stoichiometric factors γ_ρ as the smallest integers.

As an example illustrating the evaluation of γ_ρ , consider the generation of a complete set of RERs for the system $\{\text{K}^+, \text{H}_4\text{SiO}_4, \text{H}_2\text{O}, \text{H}^+, \text{Al(OH)}_3, \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4, \text{and KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2\}$. It is convenient to select the “elements” as the ions, i.e., K^+ , Al^{3+} , H^+ , Si^{4+} , and O^{2-} . This gives the following formula matrix

$$\epsilon = \begin{array}{ccccc|l} \text{K}^+ & \text{Al}^{3+} & \text{H}^+ & \text{Si}^{4+} & \text{O}^{2-} & \\ \hline 1 & 0 & 0 & 0 & 0 & \text{K} \\ 0 & 0 & 4 & 1 & 4 & \text{H}_4\text{SiO}_4 \\ 0 & 0 & 2 & 0 & 1 & \text{H}_2\text{O} \\ 0 & 0 & 1 & 0 & 0 & \text{H}^+ \\ 0 & 1 & 3 & 0 & 3 & \text{Al(OH)}_3 \\ 0 & 2 & 4 & 2 & 9 & \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \\ 1 & 3 & 2 & 3 & 12 & \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 \end{array}$$

Rank $\epsilon = 5$ and, hence, by definition, a RER involves no more than $5 + 1 = 6$ species. Because 6 species may be selected from a total of 7, in 7 different ways, the number of RERs does not exceed 7. For instance, the first 6 species define the following RER

$$\rho'(K^+, H_4SiO_4, H_2O, H^+, Al(OH)_3, \text{ and } Al_2Si_2O_5(OH)_4) =$$

$$\begin{vmatrix} 1 & 0 & 0 & 0 & 0 & K^+ \\ 0 & 0 & 4 & 1 & 4 & H_4SiO_4 \\ 0 & 0 & 2 & 0 & 1 & H_2O \\ 0 & 0 & 1 & 0 & 0 & H^+ \\ 0 & 1 & 3 & 0 & 3 & Al(OH)_3 \\ 0 & 2 & 4 & 2 & 9 & Al_2Si_2O_5(OH)_4 \end{vmatrix}$$

$$= 0K^+ + 2H_4SiO_4 - 5H_2O + H^+ + 2Al(OH)_3 -$$

$$Al_2Si_2O_5(OH)_4 = 0$$

Because the stoichiometric coefficients in this RER are equal to the smallest integers, its stoichiometric factor is equal to one. Notice that the stoichiometric coefficients of K^+ and H_2O happened to be equal to zero. For this reason, there are two more RERs that are stoichiometrically equivalent to the above RER, namely

$$\rho'(K^+, H_4SiO_4, H_2O, Al(OH)_3,$$

$$Al_2Si_2O_5(OH)_4, \text{ and } KAl_3Si_3O_{10}(OH)_2) =$$

$$\begin{vmatrix} 1 & 0 & 0 & 0 & 0 & K^+ \\ 0 & 0 & 4 & 1 & 4 & H_4SiO_4 \\ 0 & 0 & 2 & 0 & 1 & H_2O \\ 0 & 1 & 3 & 0 & 3 & Al(OH)_3 \\ 0 & 2 & 4 & 2 & 9 & Al_2Si_2O_5(OH)_4 \\ 1 & 3 & 2 & 3 & 12 & KAl_3Si_3O_{10}(OH)_2 \end{vmatrix}$$

$$= 0K^+ - 2H_4SiO_4 + 5H_2O - 2Al(OH)_3 +$$

$$Al_2Si_2O_5(OH)_4 + 0KAl_3Si_3O_{10}(OH)_2 = 0$$

$$\rho'(H_4SiO_4, H_2O, H^+, Al(OH)_3,$$

$$Al_2Si_2O_5(OH)_4, \text{ and } KAl_3Si_3O_{10}(OH)_2) =$$

$$\begin{vmatrix} 0 & 0 & 4 & 1 & 4 & H_4SiO_4 \\ 0 & 0 & 2 & 0 & 1 & H_2O \\ 0 & 1 & 3 & 0 & 3 & H^+ \\ 0 & 0 & 1 & 0 & 0 & Al(OH)_3 \\ 0 & 2 & 4 & 2 & 9 & Al_2Si_2O_5(OH)_4 \\ 1 & 3 & 2 & 3 & 12 & KAl_3Si_3O_{10}(OH)_2 \end{vmatrix}$$

$$= -2H_4SiO_4 + 5H_2O + 0H^+ - 2Al(OH)_3 +$$

$$Al_2Si_2O_5(OH)_4 + 0KAl_3Si_3O_{10}(OH)_2 = 0$$

The stoichiometric factors of these two RERs are also equal to one. Because all of these three RERs are stoichiometrically identical, the same RER in fact will occur in eq 19 exactly 3 times. It is, therefore, convenient to consider this RER just once but with a stoichiometric factor of 3. Notice also that in eq 19 the stoichiometric factors of stoichiometrically identical RERs need to be summed as γ_ρ^2 .

References and Notes

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