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Thermodynamic Stability Relations in Redox Systems

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Graphical stability relations in redox systems known as Pourbaix diagrams are analyzed employing the concept of overall stability of chemical species in multiple chemical reaction systems recently developed by us (Fishtik, I. *J. Phys. Chem. B* **2005**, *109*, 3851). The overall stability approach provides a simple and systematic algorithm for generating thermodynamically and stoichiometrically consistent Pourbaix diagrams that are referred to as overall Pourbaix diagrams. The conditions under which the conventional Pourbaix diagrams coincide with the overall Pourbaix diagrams are also discussed.

Introduction

Thermodynamic analysis is a valuable and powerful tool in predicting, comprehending, and rationalizing the stability relations in redox reaction systems. To simplify the treatment and, at the same time, enhance the visual factor, the stability relations are often analyzed employing graphical methods, i.e., by plotting the stability fields of chemical species as a function of the variables that determine the position of the electrochemical equilibrium. Clearly, for redox reaction systems of special interest is the effect of potential E and species activities, in particular, pH. Thus, the graphical, 2D constructions, delineating the stability fields of species in the coordinates E − pH and known as Pourbaix diagrams (*1*), are widely used in various areas, especially in corrosion, geochemistry, and soil science. The construction of Pourbaix diagrams as well as their various extensions has been extensively discussed in the literature (*2*−*8*). Several commercial software packages that generate Pourbaix diagrams are also available (*9*−*11*).

Despite the large variety of methodologies employed in the construction of Pourbaix diagrams, the underlying thermodynamic principles are always the same. First, the construction of a Pourbaix diagram employs a simple thermodynamic principle according to which a redox reaction is proceeding to the left or to the right depending on its sign of the Gibbs free energy. More specifically, the products in a redox reaction are stable if the Gibbs free energy change is negative. On the contrary, if the Gibbs free energy is positive, the reactants are stable. Thus, the equilibrium line separates the stability fields of the reactants and products. This simple thermodynamic principle valid for one redox reaction is next generalized to multiple redox reaction systems by applying it simultaneously to a special set of redox reactions involving in a combinatorial manner a certain number of species comprising the system. For instance, for systems comprising species of one element, the redox reactions are generated for all possible pairs of species while the electrons, hydrogen ions, and water molecules are the species used to balance the reactions. Finally, a set of rules is formulated aimed to determine the stable lines and triple points.

At first glance the conventional methodologies of constructing the Pourbaix diagrams are both thermodynamically and stoichiometrically consistent. A closer look at the problem, however, reveals that in multiple chemical reaction systems the interrelation between thermodynamic stability and stoichiometry is not trivial. As far as we are aware, the exact interrelationship between stability and stoichiometry in multiple redox reaction systems has never been discussed. In the meantime, for stability analysis this interrelationship is crucial. Indeed, stability relations based on an arbitrary set of redox reactions will inevitably result into arbitrary and, ultimately, meaningless Pourbaix diagrams. Whereas for systems comprising species of only one element (besides electrons, hydrogen, and oxygen) the redox reactions used to construct a Pourbaix diagram are trivially unique (only two species are allowed in a reaction apart from electrons, hydrogen ions, and water), for multi-element systems the conventional stability analysis formalism does not stipulate a clear algorithm for generating a unique set of reactions that should be used to deduce the stability relations. On a more general level, as well-known, conventional chemical thermodynamics itself does not provide a means to select a set of reactions out of an infinity of permitted sets.

Recently (*12*−*13*) we developed a general thermodynamic approach to the stability relations in multiple chemical reaction systems. Our main finding was a quantitative measure of stability of chemical species that has the remarkable property of being partitioned into a sum of contributions coming from a stoichiometrically unique set of reactions. These reactions were previously deduced from chemical thermodynamics and were referred to as response reactions (RERs) (*14*). We are thus in a position to formulate a unique quantitative interrelation between stability relations and stoichiometry that not only provides a simple algorithm for generating various types of thermodynamically and stoichiometrically consistent stability relations but, concomitantly, clearly shows the limitations of the conventional stability analysis. The purpose of this article is to apply this new approach to the analysis of stability relations in redox reaction systems, i.e., to the construction of Pourbaix diagrams.

Notation and Definitions

We consider a redox reaction system comprising an ideal aqueous solution and a given number of pure solid phases. The aqueous solution is assumed to contain dissolved ionic and molecular species. For reasons that will become clear later on it is convenient to consider separately three species, namely, e^- (electron), H^+ (aq), and H_2O (l). The remaining species, both dissolved and solid phases, are denoted by B_i ($i = 1, 2, ..., n$). Although our approach to the stability analysis is general, for simplicity, we assume the species to involve only four elements whereby "element" means any molecular or ionic species from which the species may be "built". To define the formula matrix we observe that three elements, namely, e^-, H, and O, have already been specified. The additional element involved in species B_i is denoted by M and, hence, the formula matrix is

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$$\epsilon = \begin{array}{cc} \begin{array}{cccc} \mathrm{e}^- & \mathrm{H} & \mathrm{O} & \mathrm{M} \end{array} & \\ \left[\begin{array}{cccc} 1 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 2 & 1 & 0 \\ \epsilon_{1,\mathrm{e}} & \epsilon_{1,\mathrm{H}} & \epsilon_{1,\mathrm{O}} & \epsilon_{1,\mathrm{E}} \\ \epsilon_{2,\mathrm{e}} & \epsilon_{2,\mathrm{H}} & \epsilon_{2,\mathrm{O}} & \epsilon_{2,\mathrm{E}} \\ \dots & \dots & \dots & \dots \\ \epsilon_{n,\mathrm{e}} & \epsilon_{n,\mathrm{H}} & \epsilon_{n,\mathrm{O}} & \epsilon_{n,\mathrm{E}} \end{array}\right] & \begin{array}{c} \mathrm{e}^- \\ \mathrm{H}^+ \\ \mathrm{H_2O} \\ \mathrm{B}_1 \\ \mathrm{B}_2 \\ \dots \\ \mathrm{B}_n \end{array} \end{array} \tag{1}$$

where $\epsilon_{i,\mathrm{e}}$, $\epsilon_{i,\mathrm{H}}$, $\epsilon_{i,\mathrm{O}}$, and $\epsilon_{i,\mathrm{E}}$ are the number of e^-, H^+, O, and M in the species B_i. Since the element M is present in all species B_i it is obvious that rank $\epsilon = 4$.

Next, we define and generate a set of response reactions (RERs) such that e^-, H^+, and H_2O are always among the species involved in a RER. Since, by definition (*14*), a RER involves no more than rank $\epsilon + 1 = 4 + 1 = 5$ species, and three species, namely, e^-, H^+, and H_2O, are always among them, to define a RER it is necessary to specify only 2 species from a total of n species B_i ($i = 1, 2, ..., n$). If these 2 species are B_p and B_q where p and q are integers satisfying the conditions $1 \le p < q \le n$, the RER is denoted by $\rho(B_p,B_q)$ and its general equation is

$$\rho(\mathrm{B}_p,\mathrm{B}_q) = z_\rho \mathrm{e}^- + h_\rho \mathrm{H}^+ + w_\rho \mathrm{H_2O} + \nu_{\rho,p}\mathrm{B}_p + \nu_{\rho,q}\mathrm{B}_q = 0 \tag{2}$$

where

$$z_\rho = \begin{vmatrix} 1 & 0 & 0 & 0 & 1 \\ -1 & 1 & 0 & 0 & 0 \\ 0 & 2 & 1 & 0 & 0 \\ \epsilon_{p,\mathrm{e}} & \epsilon_{p,\mathrm{H}} & \epsilon_{p,\mathrm{O}} & \epsilon_{p,\mathrm{E}} & 0 \\ \epsilon_{q,\mathrm{e}} & \epsilon_{q,\mathrm{H}} & \epsilon_{q,\mathrm{O}} & \epsilon_{q,\mathrm{E}} & 0 \end{vmatrix} h_\rho = \begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 1 \\ 0 & 2 & 1 & 0 & 0 \\ \epsilon_{p,\mathrm{e}} & \epsilon_{p,\mathrm{H}} & \epsilon_{p,\mathrm{O}} & \epsilon_{p,\mathrm{E}} & 0 \\ \epsilon_{q,\mathrm{e}} & \epsilon_{q,\mathrm{H}} & \epsilon_{q,\mathrm{O}} & \epsilon_{q,\mathrm{E}} & 0 \end{vmatrix}$$

$$w_\rho = \begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 \\ 0 & 2 & 1 & 0 & 1 \\ \epsilon_{p,\mathrm{e}} & \epsilon_{p,\mathrm{H}} & \epsilon_{p,\mathrm{O}} & \epsilon_{p,\mathrm{E}} & 0 \\ \epsilon_{q,\mathrm{e}} & \epsilon_{q,\mathrm{H}} & \epsilon_{q,\mathrm{O}} & \epsilon_{q,\mathrm{E}} & 0 \end{vmatrix} \nu_{\rho,p} = \begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 \\ 0 & 2 & 1 & 0 & 0 \\ \epsilon_{p,\mathrm{e}} & \epsilon_{p,\mathrm{H}} & \epsilon_{p,\mathrm{O}} & \epsilon_{p,\mathrm{E}} & 1 \\ \epsilon_{q,\mathrm{e}} & \epsilon_{q,\mathrm{H}} & \epsilon_{q,\mathrm{O}} & \epsilon_{q,\mathrm{E}} & 0 \end{vmatrix}$$

$$\nu_{\rho,q} = \begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 \\ 0 & 2 & 1 & 0 & 0 \\ \epsilon_{p,\mathrm{e}} & \epsilon_{p,\mathrm{H}} & \epsilon_{p,\mathrm{O}} & \epsilon_{p,\mathrm{E}} & 0 \\ \epsilon_{q,\mathrm{e}} & \epsilon_{q,\mathrm{H}} & \epsilon_{q,\mathrm{O}} & \epsilon_{q,\mathrm{E}} & 1 \end{vmatrix}$$

The Gibbs free energy changes of the RERs at specified temperature T, pressure P, and composition (activities) a_{e^-}, a_{H^+}, a_{H_2O}, a_{B_i} ($i = 1, 2, ..., n$) are given by

$$\Delta G_\rho = \Delta G_\rho^0(T,P) + z_\rho RT\ln a_{\mathrm{e}^-} + h_\rho RT\ln a_{\mathrm{H}^+} + w_\rho RT\ln a_{\mathrm{H_2O}} + \nu_{\rho,p}RT\ln a_{\mathrm{B}_p} + \nu_{\rho,q}RT\ln a_{\mathrm{B}_q} \tag{3}$$

Introducing the electrode potential E and pH according to

$$E = -\frac{RT}{F}\ln a_{e^-} \tag{4}$$

$$\mathrm{pH} = -\log a_{\mathrm{H}^+} \tag{5}$$

where F is the Faraday constant and taking into account that the aqueous solution is assumed ideal ($a_{H_2O} = 1$), eq 3 may be written as

$$\Delta G_\rho = \Delta G_\rho^0(T,P) - z_\rho FE - 2.3h_\rho RT\mathrm{pH} + \nu_{\rho,p}RT\ln a_{\mathrm{B}_p} + \nu_{\rho,q}RT\ln a_{\mathrm{B}_q} \tag{6}$$

In generating the RERs and their Gibbs free energy changes we accept the convention according to which the stoichiometric coefficients in RERs are selected as the smallest integers. In this case, every RER is characterized by a stoichiometric factor γ_ρ (*12*).

The number of RERs is equal to the number of ways two species B_i may be selected from a total of n, that is, $n(n - 1)/2$. Clearly, only $n - 1$ of them are linearly independent. Without loss of generality, we choose a subset of linearly independent RERs as

$$\rho_1 = \rho(\mathrm{B}_1,\mathrm{B}_2) = z_1\mathrm{e}^- + h_1\mathrm{H}^+ + w_1\mathrm{H_2O} + \nu_{11}\mathrm{B}_1 + \nu_{12}\mathrm{B}_2 = 0$$

$$\rho_2 = \rho(\mathrm{B}_1,\mathrm{B}_3) = z_2\mathrm{e}^- + h_2\mathrm{H}^+ + w_2\mathrm{H_2O} + \nu_{21}\mathrm{B}_1 + \nu_{23}\mathrm{B}_3 = 0$$

...

$$\rho_{n-1} = \rho(\mathrm{B}_1,\mathrm{B}_n) = z_{n-1}\mathrm{e}^- + h_{n-1}\mathrm{H}^+ + w_{n-1}\mathrm{H_2O} + \nu_{n-1,1}\mathrm{B}_1 + \nu_{n-1,n}\mathrm{B}_n = 0 \tag{7}$$

The stoichiometric coefficients of the species B_i in this set of linearly independent RERs are collected into a separate stoichiometric submatrix

$$\boldsymbol{\nu} = \begin{array}{cc} \begin{array}{ccccc} \mathrm{B}_1 & \mathrm{B}_2 & \mathrm{B}_3 & \dots & \mathrm{B}_n \end{array} & \\ \left[\begin{array}{ccccc} \nu_{11} & \nu_{12} & 0 & \dots & 0 \\ \nu_{21} & 0 & \nu_{13} & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \nu_{n-1,1} & 0 & 0 & \dots & \nu_{n-1,n} \end{array}\right] & \begin{array}{c} \rho_1 \\ \rho_2 \\ \dots \\ \rho_{n-1} \end{array} \end{array} \tag{8}$$

Finally, we define a vector of the Gibbs free energy changes of the independent reactions

$$\Delta\mathbf{G} = (\Delta G_1,\Delta G_2,\dots,\Delta G_{n-1})^{\mathrm{t}} \tag{9}$$

where t stands for transposition.

Conventional Pourbaix Diagrams

In terms of RERs, the construction of a conventional Pourbaix diagram may be briefly formulated as follows (*1*). The stability fields of two species say, B_p and B_q, in coordinates E − pH at given T, P and species activities are separated by the straight line

$$\Delta G_{\rho(\mathrm{B_p,B_q})}\ (E,\mathrm{pH}) = 0 \tag{10}$$

while the triple points, i.e., the intersection of three lines separating the stability fields of three species say, B_p, B_q, and B_r, are determined by solving simultaneously a linear systems of equations

$$\Delta G_{\rho(\mathrm{B_p,B_q})}\ (E,\mathrm{pH}) = \Delta G_{\rho(\mathrm{B_p,B_r})}\ (E,\mathrm{pH}) = \Delta G_{\rho(\mathrm{B_q,B_r})}\ (E,\mathrm{pH}) = 0 \tag{11}$$

Employing various mathematical and numerical techniques, eqs 10 and 11 are next analyzed for the evaluation of stable/metastable lines and intersections. For instance, in computer software, such as FactSage (*10*), the construction of the Pourbaix diagram is based on a numerical procedure called

Gibbs energy minimization (not to be confused with the evaluation of the chemical equilibrium via the direct minimization of the Gibbs free energy). Within this method a subset of linearly independent RERs, eq 7, is selected such that the species B_1 is the most stable allotropic form of the element M under standard conditions. The Gibbs free energy changes of these reactions are next numerically evaluated as a function of E and pH. At a particular point in the plane E − pH, the species involved in the reaction with the lowest Gibbs free energy change is considered to be stable.

It should be noted that the conventional Pourbaix diagrams are subject to a serious thermodynamic limitation. Namely, when constructing a Pourbaix diagram it is tacitly assumed that the activities of e^-, H^+, and H_2O are equal to their equilibrium values. In other words, these species are ruled out from the thermodynamic analysis (*12*). While for dilute aqueous solutions the amount of H_2O remains constant, this is certainly not the case for e^- and H^+. Our approach is general and does not require any assumptions concerning the activities of species. In what follows, however, we will assume that the activities of e^-, H^+, and H_2O are equal to their equilibrium values. This is done only for the purpose of obtaining Pourbaix diagrams that are compatible with the conventional ones.

Overall Stability of the Species

We present next a succinct review of our overall stability approach. For details the reader is referred to our previous publications (*12*, *13*). The main idea of the overall stability analysis is to define a *quantitative* measure of the stability. Let $\bar{G}_{e^-}$, $\bar{G}_{H^+}$, $\bar{G}_{H_2O}$, $\bar{G}_{B_i}$ ($i = 1,2,...,n$) be the partial Gibbs free energies of the species in the initial state of the system, while the same quantities in the equilibrium state will be $\bar{G}^{eq}_{e^-}$, $\bar{G}^{eq}_{H^+}$, $\bar{G}^{eq}_{H_2O}$, $\bar{G}^{eq}_{B_i}$ ($i = 1,2,...,n$). Now, it appears that a natural choice of the stability measure of the species is just the difference between the partial Gibbs free energy of a species in the initial and equilibrium state. We, therefore, define an overall stability for every species as

$$\Sigma_{e^-} = \bar{G}_{e^-} - \bar{G}^{eq}_{e^-} \tag{12}$$

$$\Sigma_{H^+} = \bar{G}_{H^+} - \bar{G}^{eq}_{H^+} \tag{13}$$

$$\Sigma_{H_2O} = \bar{G}_{H_2O} - \bar{G}^{eq}_{H_2O} \tag{14}$$

$$\Sigma_{Bi} = \bar{G}_{Bi} - \bar{G}^{eq}_{Bi};\ (i = 1,2,...,n) \tag{15}$$

According to this definition a species is considered stable if its overall stability is negative. On the contrary, if the overall stability is positive, a species is unstable. If the overall stability is equal to zero a species is at equilibrium. To generate stability diagrams that are compatible with the conventional Pourbaix diagrams we further assume that the overall stabilities of e^-, H^+, and H_2O are equal to zero and, thus, the analysis is focused only on the overall stability of the species B_i. Based on our previous results, it may be shown that under these conditions the overall stabilities of the species B_i are given by

$$\mathbf{\Sigma} = \boldsymbol{\nu}^{T}(\boldsymbol{\nu}\boldsymbol{\nu}^{T})^{-1}\Delta\mathbf{G} \tag{16}$$

where $\boldsymbol{\nu}$ and $\Delta\mathbf{G}$ are given by eqs 8 and 9 and Σ is the overall stability vector

$$\mathbf{\Sigma} = (\Sigma_{B_1},\Sigma_{B_2},...,\Sigma_{B_n})^{t} \tag{17}$$

The overall stabilities have the important property of being uniquely partitioned into contributions coming from RERs as follows

$$\Sigma_{Bi} = \frac{1}{D}\sum_{\rho}\gamma_{\rho}^{2}\nu_{\rho,i}\Delta G_{\rho} \tag{18}$$

where

$$D = \frac{1}{n-1}\sum_{\rho}\sum_{i=1}^{n}\gamma_{\rho}^{2}\nu_{\rho,i}^{2} \tag{19}$$

The summation in eqs 18 and 19 runs over a complete set of RERs. Since the RERs are stoichiometrically unique, the independence of the overall stability vector Σ in eq 16 on the choice of ν is self-evident.

Overall Pourbaix Diagrams

The overall stability approach may be regarded as an exact and quantitative formulation of the stability relations in redox reaction systems. Concomitantly, the overall stability approach provides an algorithm to generate thermodynamically and stoichiometrically consistent Pourbaix diagrams. In what follows, the Pourbaix diagrams generated based on the overall stabilities of the species are referred to as overall Pourbaix diagrams. Since the overall stabilities of the species may be evaluated numerically at any point in the plane E − pH the construction of an overall Pourbaix diagram is straightforward and is based on the following considerations:

(a) A species, say B_p, is dominant in a certain region of the plane E − pH if its overall stability $\Sigma_{B_p}(E,\text{pH})$ in this region is nonpositive and lower than the overall stability of any other species.

(b) The stability fields of two species, say B_p and B_q, are separated by a straight line, called predominance line, such that the overall stabilities of B_p and B_q at each point on this line are nonpositive and equal, i.e., $\Sigma_{B_p}(E,\text{pH}) = \Sigma_{B_q}(E,\text{pH})$. A predominance line separating the stability fields of two species B_p and B_q is stable if their overall stabilities on the predominance line are nonpositive, equa, and lower than the overall stabilities of any other species.

(c) The stability fields of three species, say B_p, B_q, and B_r, intersects at a point, called the triple point, such that the overall stability of the species B_p, B_q, and B_r at this point are nonpositive and equal, i.e., $\Sigma_{B_p}(E,\text{pH}) = \Sigma_{B_q}(E,\text{pH}) = \Sigma_{B_r}(E,\text{pH})$. A triple point is stable if the overall stabilities of the species B_p, B_q, and B_r at this point are nonpositive, equal, and lower than the overall stabilities of any other species.

The easiest way to construct an overall Pourbaix diagram is to generate first the stable triple points. The latter may be found by checking for stability all possible triple points, i.e., solving the equations $\Sigma_{B_p}(E,\text{pH}) = \Sigma_{B_q}(E,\text{pH}) = \Sigma_{B_r}(E,\text{pH})$ for all possible combinations of 3 species from a total on n. Once the location of the stable triple points is known, the final topology of the stability fields of the species may be deduced by determining the stable predominance lines. Alternatively, one can plot the overall stabilities of all species as planes in a three-dimensional space Σ_{B_i} − E − pH and bearing in mind that on a 3D overall Pourbaix diagram only the planes with the lowest value of the overall stability should be present.

Conventional vs Overall Pourbaix Diagrams

We are now in a position to formulate the interrelation between the conventional and overall Pourbaix diagrams. From the above developments it follows that within the overall stability analysis a species B_i is stable in a certain

TABLE 1. List of Species and Their Gibbs Free Energy of Formation at Standard Conditions in the System $E^- - H - O - Fe$ (Data from Ref *11*)

species	ΔG_f^0 kcal/mol
1. e(aq)	0.00
2. H^+(aq)	0.00
3. H_2O(l)	−56.68
4. Fe(s)	0.00
5. Fe^{2+}(aq)	−21.88
6. Fe^{3+}(aq)	−4.11
7. $Fe(OH)_2$(s)	−116.39
8. $Fe(OH)_3$(s)	−166.46
9. Fe_3O_4(s)	−242.65

region of the plane $E - \text{pH}$ if its overall stability $\Sigma_{B_i}(E,\text{pH})$ satisfies the conditions

$$\Sigma_{B_i}(E,\text{pH}) = \frac{1}{D}\sum_{\rho}\gamma_{\rho}^2\nu_{\rho,i}\Delta G_{\rho}(E,\text{pH}) \leq 0 \qquad (20)$$

$$\Sigma_{B_i}(E,\text{pH}) \leq \Sigma_{B_j}(E,\text{pH})\ (j = 1,2,...,i-1,i+1,...,n) \qquad (21)$$

According to the conventional stability analysis a species is considered stable if eq 20 is satisfied. However, within the conventional approach the species stabilities are subject to a more restrictive condition. Namely, every term in eq 20 is required to be nonpositive. Since γ_{ρ}^2 and D are positive, the conventional stability analysis requires

$$\Sigma_{B_i}(E,\text{pH}) = \frac{1}{D}\sum_{\rho}\gamma_{\rho}^2\nu_{\rho,i}\Delta G_{\rho}(E,\text{pH}) \leq 0 \qquad (20)$$

$$\nu_{\rho,i}\Delta G_{\rho}(E,\text{pH}) \leq 0 \text{ for all } \rho \text{ involving } B_i \qquad (22)$$

On the basis of this analysis we conclude the following. If the ratio $\epsilon_{p,E}/\epsilon_{q,E}$ $(1 \leq p < q \leq n)$ is equal to one for all pairs of species B_p and B_q, or, more restrictively, if all entries in the stoichiometric submatrix ν are equal to ±1, the conventional and overall Pourbaix diagrams *coincide*. On the contrary, if the ratio $\epsilon_{p,E}/\epsilon_{q,E}$ $(1 \leq p < q \leq n)$ is different from one at least for one pair of species B_p and B_q, the conventional and overall Pourbaix diagram may *differ*. A more concise and general formulation of the second part of the above statement is hardly possible because of the complexity of the stoichiometry. The proof of the first part, although elementary, is very cumbersome and is omitted. Rather, we will illustrate the above findings with the help of an example.

An Example

As an example illustrating the theoretical developments presented above we consider the stability relations in the system $e^- - H - O - Fe$. The list of species along with their Gibbs free energies of formation is presented in Table 1. First, we consider the subsystem $e^-(aq) - H^+(aq) - H_2O(l) - Fe(s) - Fe^{2+}(aq) - Fe^{3+}(aq) - Fe(OH)_2(s) - Fe(OH)_3(s)$. As can be seen, for this subsystem $\epsilon_{i,Fe} = 1$ for all Fe species and, consequently, the conventional and overall Pourbaix diagrams should coincide. The conventional Pourbaix diagram is constructed based on the analysis of a complete set of RERs. These may be generated according to eq 2 and are presented in Table 2 (first 10 RERs). Since the construction of the conventional Pourbaix diagram (Figure 1) is well documented we consider here only the construction of the overall Pourbaix diagram.

Our starting point is a set of linearly independent reactions that we arbitrarily select as the first four RERs from the list of RERs (Table 2)

$$\rho_1 = 2e^- - Fe + Fe^{2+} = 0$$

$$\rho_2 = 3e^- - Fe + Fe^{3+} = 0$$

$$\rho_3 = 2e^- + 2H^+ - 2H_2O - Fe + Fe(OH)_2 = 0$$

$$\rho_4 = 3e^- + 3H^+ - 3H_2O - Fe + Fe(OH)_3 = 0$$

Assuming, for simplicity, that the activities of Fe^{2+} and Fe^{3+} are equal to one, the Gibbs free energy changes of these reactions are

$$\Delta G_1 = \Delta G_1^0 - 2FE$$

$$\Delta G_2 = \Delta G_2^0 - 3FE$$

$$\Delta G_3 = \Delta G_3^0 - 2 \times 2.3RT\,\text{pH} - 2FE$$

$$\Delta G_4 = \Delta G_4^0 - 3 \times 2.3RT\,\text{pH} - 3FE$$

Thus, the stoichiometric submatrix ν and the Gibbs free energy changes vector $\Delta\mathbf{G}$ are

$$\boldsymbol{\nu} = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 1 & 0 \\ -1 & 0 & 0 & 0 & 1 \end{bmatrix};\ \Delta\mathbf{G} = \begin{bmatrix} \Delta G_1 \\ \Delta G_2 \\ \Delta G_3 \\ \Delta G_4 \end{bmatrix}$$

TABLE 2. Complete List of RERs, Their Stoichiometric Factors, and Gibbs Free Energy Changes at Standard Conditions for the System the $e^- - H - O - Fe$

RERs	γ_j^2	$\Delta G_j/F$
$\rho_1 = 2e^- - Fe + Fe^{2+} = 0$	1	$-0.949 - 2E$
$\rho_2 = 3e^- - Fe + Fe^{3+} = 0$	1	$-0.178 - 3E$
$\rho_3 = 2e^- + 2H^+ - 2H_2O - Fe + Fe(OH)_2 = 0$	1	$-0.131 - 0.118\text{pH} - 2E$
$\rho_4 = 3e^- + 3H^+ - 3H_2O - Fe + Fe(OH)_3 = 0$	1	$0.155 - 0.177\text{pH} - 3E$
$\rho_5 = e^- - Fe^{2+} + Fe^{3+} = 0$	1	$0.771 - E$
$\rho_6 = 2H^+ - 2H_2O - Fe^{2+} + Fe(OH)_2 = 0$	1	$0.817 - 0.118\text{pH}$
$\rho_7 = e^- + 3H^+ - 3H_2O - Fe^{2+} + Fe(OH)_3 = 0$	1	$1.104 - 0.177\text{pH} - E$
$\rho_8 = e^- - 2H^+ + 2H_2O + Fe^{3+} - Fe(OH)_2 = 0$	1	$-0.047 + 0.118\text{pH} - E$
$\rho_9 = 3H^+ - 3H_2O - Fe^{3+} + Fe(OH)_3 = 0$	1	$0.333 - 0.177\text{pH}$
$\rho_{10} = e^- + H^+ - H_2O - Fe(OH)_2 + Fe(OH)_3 = 0$	1	$0.287 - 0.059\text{pH} - E$
$\rho_{11} = 8e^- + 8H^+ - 4H_2O - 3Fe + Fe_3O_4 = 0$	1	$-0.691 - 0.473\text{pH} - 8E$
$\rho_{12} = 2e^- + 8H^+ - 4H_2O - 3Fe^{2+} + Fe_3O_4 = 0$	1	$2.156 - 0.473\text{pH} - 2E$
$\rho_{13} = e^- - 8H^+ + 4H_2O + 3Fe^{3+} - Fe_3O_4 = 0$	1	$0.156 + 0.473\text{pH} - E$
$\rho_{14} = 2e^- + 2H^+ + 2H_2O - 3Fe(OH)_2 + Fe_3O_4 = 0$	1	$-0.297 - 0.118\text{pH} - 2E$
$\rho_{15} = e^- + H^+ - 5H_2O + 3Fe(OH)_3 - Fe_3O_4 = 0$	1	$1.157 - 0.059\text{pH} - E$

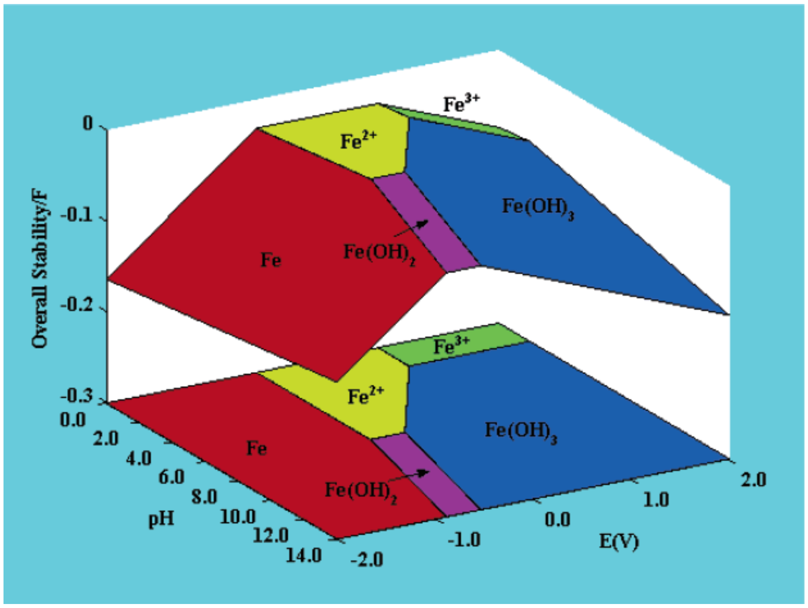

FIGURE 1. Pourbaix diagram for the system $e^-(aq) - H^+(aq) - H_2O(l) - Fe(s) - Fe^{2+}(aq) - Fe^{3+}(aq) - Fe(OH)_2(s) - Fe(OH)_3(s)$. The overall Pourbaix diagram is presented in a three-dimensional space.

Substituting these into eq 16 and performing the matrix operations gives

$$\Sigma_{Fe} = 1/5(-\Delta G_1 - \Delta G_2 - \Delta G_3 - \Delta G_4)$$

$$\Sigma_{Fe^{2+}} = 1/5(4\Delta G_1 - \Delta G_2 - \Delta G_3 - \Delta G_4)$$

$$\Sigma_{Fe^{3+}} = 1/5(-\Delta G_1 + 4\Delta G_2 - \Delta G_3 - \Delta G_4)$$

$$\Sigma_{Fe(OH)_2} = 1/5(-\Delta G_1 - \Delta G_2 + 4\Delta G_3 - \Delta G_4)$$

$$\Sigma_{Fe(OH)_3} = 1/5/(-\Delta G_1 - \Delta G_2 - \Delta G_3 + 4\Delta G_4)$$

Now, employing these overall stabilities it may be easily shown that the overall and conventional Pourbaix diagrams for this subsystem coincide. Consider several examples. Thus, according to the conventional approach the predominance fields of Fe and Fe^{2+} are separated by the line $\Delta G_1(E,\text{pH}) = 0$. According to the overall stability approach the predominance fields of Fe and Fe^{2+} are separated by the predominance line $\Sigma_{Fe}(E,\text{pH}) = \Sigma_{Fe^{2+}}(E,\text{pH})$, or, $\Sigma_{Fe}(E,\text{pH}) - \Sigma_{Fe^{2+}}(E,\text{pH}) = 0$. Solving this equation gives precisely $\Delta G_1(E,\text{pH}) = 0$. Similarly, the predominance line separating the stability fields of Fe and $Fe(OH)_2$ according to the conventional approach is given by $\Delta G_3(E,\text{pH}) = 0$. Equating the overall stabilities of Fe and $Fe(OH)_2$ results in exactly the same equation. It is further obvious that the triple point $Fe - Fe^{2+} - Fe(OH)_2$ is determined within both approaches by simultaneously solving the system $\Delta G_1(E,\text{pH}) = 0$ and $\Delta G_3(E,\text{pH}) = 0$. Continuing this procedure over stability fields and their intersections for the remaining species it may be shown that for this system the overall and conventional Pourbaix diagrams coincide.

The advantage of the overall stability approach is that one can determine directly whether a certain triple point is stable or not. As an example, consider the stability of the triple point $Fe - Fe^{2+} - Fe(OH)_2$. Employing the numerical values of Gibbs free energy changes and, for simplicity, dividing the overall stabilities by the Faraday constant we obtain

$$\Sigma_{Fe}(E,\text{pH}) = 0.221 + 0.059\text{pH} + 2E$$

$$\Sigma_{Fe^{2+}}(E,\text{pH}) = -0.728 + 0.059\text{pH}$$

$$\Sigma_{Fe^{3+}}(E,\text{pH}) = 0.043 + 0.059\text{pH} - E$$

$$\Sigma_{Fe(OH)_2}(E,\text{pH}) = 0.089 - 0.059\text{pH}$$

$$\Sigma_{Fe(OH)_3}(E,\text{pH}) = 0.376 - 0.118\text{pH} - E$$

At the triple point $Fe - Fe^{2+} - Fe(OH)_2$ we have $\Sigma_{Fe}(E,\text{pH}) = \Sigma_{Fe^{2+}}(E,\text{pH}) = \Sigma_{Fe(OH)_2}(E,\text{pH})$. The solution of this system of equations is $E = -0.47$ and $\text{pH} = 6.92$ while the overall stabilities of the species at this point are equal to

$$\Sigma_{Fe} = -0.32 \quad \Sigma_{Fe(OH)_2} = -0.32$$

$$\Sigma_{Fe^{2+}} = -0.32 \quad \Sigma_{Fe(OH)_3} = 0.03$$

$$\Sigma_{Fe^{3+}} = 0.93$$

As can be seen, the overall stabilities of Fe, Fe^{2+}, and $Fe(OH)_2$ at the triple point are negative, equal, and lower than the overall stabilities of the remaining species. Hence, this triple point is stable. The methodology of construction of overall Pourbaix diagrams may be best illustrated by plotting the overall stabilities in a three-dimensional space as illustrated in Figure 1.

Let us now add $Fe_3O_4(s)$ to the above subsystem. For this species $\epsilon_{Fe_3O_4,Fe} = 3$ and the overall and conventional Pourbaix diagrams may differ. The conventional Pourbaix diagram constructed based on the analysis of the RERs given in Table 1 is presented in Figure 2. To construct the overall Pourbaix

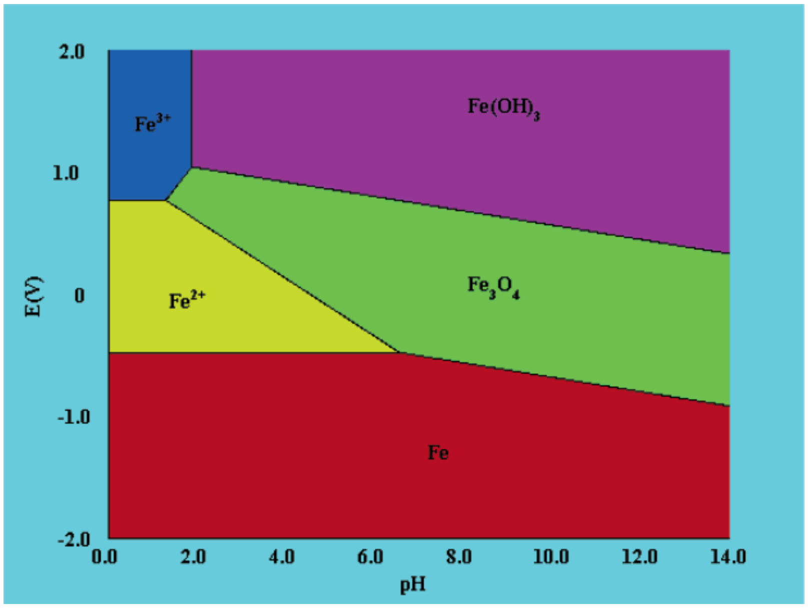

FIGURE 2. Conventional Pourbaix diagram for the system $e^-(aq) - H^+(aq) - H_2O(l) - Fe(s) - Fe^{2+}(aq) - Fe^{3+}(aq) - Fe(OH)_2(s) - Fe(OH)_3(s) - Fe_3O_4(s)$.

diagram we first select from Table 1 a set of linearly independent RERs, say

$$\rho_1 = 2e^- - Fe + Fe^{2+} = 0$$

$$\rho_2 = 3e^- - Fe + Fe^{3+} = 0$$

$$\rho_3 = 2e^- + 2H^+ - 2H_2O - Fe + Fe(OH)_2 = 0$$

$$\rho_4 = 3e^- + 3H^+ - 3H_2O - Fe + Fe(OH)_3 = 0$$

$$\rho_{11} = 8e^- + 8H^+ - 4H_2O - 3Fe + Fe_3O_4 = 0$$

The Gibbs free energy changes of these RERs are

$$\Delta G_1 = \Delta G_1^0 - 2FE$$

$$\Delta G_2 = \Delta G_2^0 - 3FE$$

$$\Delta G_3 = \Delta G_3^0 - 2 \times 2.3RT\,\mathrm{pH} - 2FE$$

$$\Delta G_4 = \Delta G_4^0 - 3 \times 2.3RT\,\mathrm{pH} - 3FE$$

$$\Delta G_{11} = \Delta G_5^0 - 8 \times 2.3RT\,\mathrm{pH} - 8FE$$

This gives the following stoichiometric submatrix ν and the Gibbs free energy changes vector $\mathbf{\Delta G}$

$$\boldsymbol{\nu} = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 & 1 & 0 \\ -3 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}; \mathbf{\Delta G} = \begin{bmatrix} \Delta G_1 \\ \Delta G_2 \\ \Delta G_3 \\ \Delta G_4 \\ \Delta G_{11} \end{bmatrix}$$

Substituting these matrixes into eq 16 and performing the respective matrix operations we obtain

$$\Sigma_{Fe} = 1/14\,(-\Delta G_1 - \Delta G_2 - \Delta G_3 + \Delta G_4 - 3\Delta G_{11})$$

$$\Sigma_{Fe^{2+}} = 1/14\,(13\Delta G_1 - \Delta G_2 - \Delta G_3 + \Delta G_4 - 3\Delta G_{11})$$

$$\Sigma_{Fe^{3+}} = 1/14\,(-\Delta G_1 + 13\Delta G_2 - \Delta G_3 + \Delta G_4 - 3\Delta G_{11})$$

$$\Sigma_{Fe(OH)_2} = 1/14\,(-\Delta G_1 - \Delta G_2 + 13\Delta G_3 + \Delta G_4 - 3\Delta G_{11})$$

$$\Sigma_{Fe(OH)_3} = 1/14\,(-\Delta G_1 - \Delta G_2 - \Delta G_3 - 13\Delta G_4 - 3\Delta G_{11})$$

$$\Sigma_{Fe_3O_4} = 1/14\,(-3\Delta G_1 - 3\Delta G_2 - 3\Delta G_3 + 3\Delta G_4 + 5\Delta G_{11})$$

or, employing the numerical values of the Gibbs free energies and dividing the overall stabilities by Faraday constant

$$\Sigma_{Fe}(E,\mathrm{pH}) = 0.227 + 0.122\mathrm{pH} + 2.429E$$

$$\Sigma_{Fe^{2+}}(E,\mathrm{pH}) = -0.722 + 0.122\mathrm{pH} + 0.429E$$

$$\Sigma_{Fe^{3+}}(E,\mathrm{pH}) = 0.049 + 0.122\mathrm{pH} - 0.571E$$

$$\Sigma_{Fe(OH)_2}(E,\mathrm{pH}) = 0.096 + 0.004\mathrm{pH} + 0.429E$$

$$\Sigma_{Fe(OH)_3}(E,\mathrm{pH}) = 0.382 - 0.055\mathrm{pH} - 0.571E$$

$$\Sigma_{Fe_3O_4}(E,\mathrm{pH}) = -0.010 - 0.106\mathrm{pH} - 0.714E$$

Now, following the algorithm presented above, the construction of the overall Pourbaix diagram is straightforward. Consider first the predominance line separating the stability fields of Fe and Fe^{2+}. Equating the overall stabilities of these two species gives $\Delta G_1 = 0$ and, consequently, this line coincides with the predominance line predicted by the conventional approach. Next, consider the predominance line separating Fe and Fe_3O_4. Solving $\Sigma_{Fe} = \Sigma_{Fe_3O_4}$ gives ΔG_1

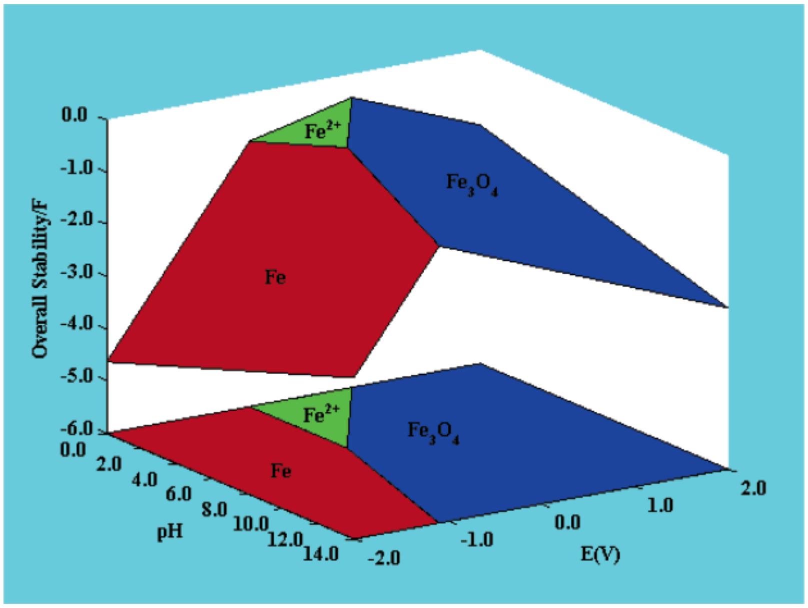

FIGURE 3. Overall Pourbaix diagram for the system $e^-(aq) - H^+(aq) - H_2O(l) - Fe(s) - Fe^{2+}(aq) - Fe^{3+}(aq) - Fe(OH)_2(s) - Fe(OH)_3(s) - Fe_3O_4(s)$.

$+ \Delta G_2 + \Delta G_3 - \Delta G_4 - 4\Delta G_{11} = 0$. Clearly, this predominance line differs from the predominance line predicted by the conventional approach, i.e., $\Delta G_{11} = 0$. Similarly, the coordinates of the triple point $Fe - Fe^{2+} - Fe_3O_4$ differ. Thus, the coordinates of this triple point within the overall stability approach are obtained by solving simultaneously the system of equations $\Sigma_{Fe}(E,pH) = \Sigma_{Fe^{2+}}(E,pH) = \Sigma_{Fe_3O_4}(E,pH)$. The result is $E = -0.47$ and pH = 5.50. The coordinates of the same triple point with the conventional stability approach are $E = -0.47$ and pH = 6.58. To determine whether this triple point is stable we evaluate numerically the overall stabilities at the triple point

$$\Sigma_{Fe} = -0.25 \quad \Sigma_{Fe(OH)_2} = -0.09$$

$$\Sigma_{Fe^{2+}} = -0.25 \quad \Sigma_{Fe(OH)_3} = 0.35$$

$$\Sigma_{Fe^{3+}} = 0.99 \quad \Sigma_{Fe_3O_4} = -0.25$$

Since the overall stabilities of Fe, Fe^{2+}, and Fe$_3$O$_4$ are negative, equal, and lower than the overall stabilities of the remaining species this triple pint is stable. The most drastic difference between the overall and conventional Pourbaix diagram, however, is that the triple point $Fe^{3+} - Fe(OH)_3 - Fe_3O_4$ is unstable according to the overall approach while the conventional approach predicts that this triple point is stable. Indeed, the solution of the system of equations $\Sigma_{Fe^{3+}}(E,pH) = \Sigma_{Fe(OH)_3}(E,pH) = \Sigma_{Fe_3O_4}(E,pH)$ gives $E = -3.41$ and pH = 1.88. The overall stabilities of the species at this point are

$$\Sigma_{Fe} = -7.83 \quad \Sigma_{Fe(OH)_2} = -1.36$$

$$\Sigma_{Fe^{2+}} = -1.96 \quad \Sigma_{Fe(OH)_3} = 2.23$$

$$\Sigma_{Fe^{3+}} = 2.23 \quad \Sigma_{Fe_3O_4} = 2.23$$

It is seen that the overall stabilities of Fe^{3+}, Fe(OH)$_3$, and Fe$_3$O$_4$ at the triple point, although equal, are positive and higher than the overall stabilities of the remaining species, thus, making this triple point unstable. As a result, the overall stability of Fe(OH)$_3$ is never dominant and this species should be eliminated from the overall Pourbaix diagram. Continuing the overall stability analysis over the remaining triple points we conclude that only two triple points from a total of 15 are stable, namely, $Fe - Fe^{2+} - Fe_3O_4$ and $Fe^{2+} - Fe^{3+} - Fe_3O_4$. The coordinates of the second of these two triple points lie in the negative region of pH and, therefore, this triple point is not shown on the final overall Pourbaix diagram presented in Figure 3. Comparing Figures 2 and 3 it can be seen that the two types of Pourbaix diagrams are topologically different.

A Graph-Theoretical Interpretation of the Overall Stability

The overall stability approach may be given a natural graph-theoretical interpretation in terms of directed bipartite graphs (*15*). According to the bipartite graph formalism a chemical reaction is described by two sets of vertexes. One of them depicts the chemical reaction itself. This vertex is connected via directed edges to another set of vertexes representing reactants and products. For the particular case of redox reactions the bipartite graph description is fairly simple since the electrons, hydrogen ions, and water molecules may be dropped from the graph. Thus, the bipartite graph of a RER $\rho(B_p,B_q)$ involves only two directed edges. Now, eq 18 may be translated into a bipartite graph network by placing the n species B_i ($i = 1, 2, ..., n$) into a set of n nodes. These nodes are mutually interconnected via a complete set of $n(n-1)/2$ nodes representing the RERs. Further, the edges interconnecting the species are appropriately weighted. Namely, the edge that is incident to species B_p in RER $\rho(B_p,B_q)$ is weighted by $\gamma_\rho^2\nu_{\rho,p}\Delta G_\rho/D$ while the edge incident to B_q is weighted by $\gamma_\rho^2\nu_{\rho,q}\Delta G_\rho/D$. Additionally, it is specified that the edges are directed from species B_p to species B_q if $\gamma_\rho^2\nu_{\rho,p}\Delta G_\rho/D > 0$ and $\gamma_\rho^2\nu_{\rho,q}\Delta G_\rho/D < 0$ and, vice versa. The bipartite graph network interpretation of the overall stability is exemplified in Figure 4 for the system $e^-(aq) - H^+(aq) - H_2O(l) - Fe(s) - Fe^{2+}(aq) - Fe^{3+}(aq) - Fe(OH)_2(s) - Fe(OH)_3(s) - Fe_3O_4(s)$.

The bipartite graph network interpretation of the overall stability is especially useful in connection with the widespread availability of computer graphics. Indeed, because the Gibbs free energies of the RERs $\Delta G_\rho(E,pH)$ are analytical functions of E and pH, each species in a bipartite graph network may be assigned a color characteristic as a function of E and pH that is associated to its overall stability. Similarly, the thickness of directed edges may be linked to $\Delta G_\rho(E,pH,)$ thus allowing

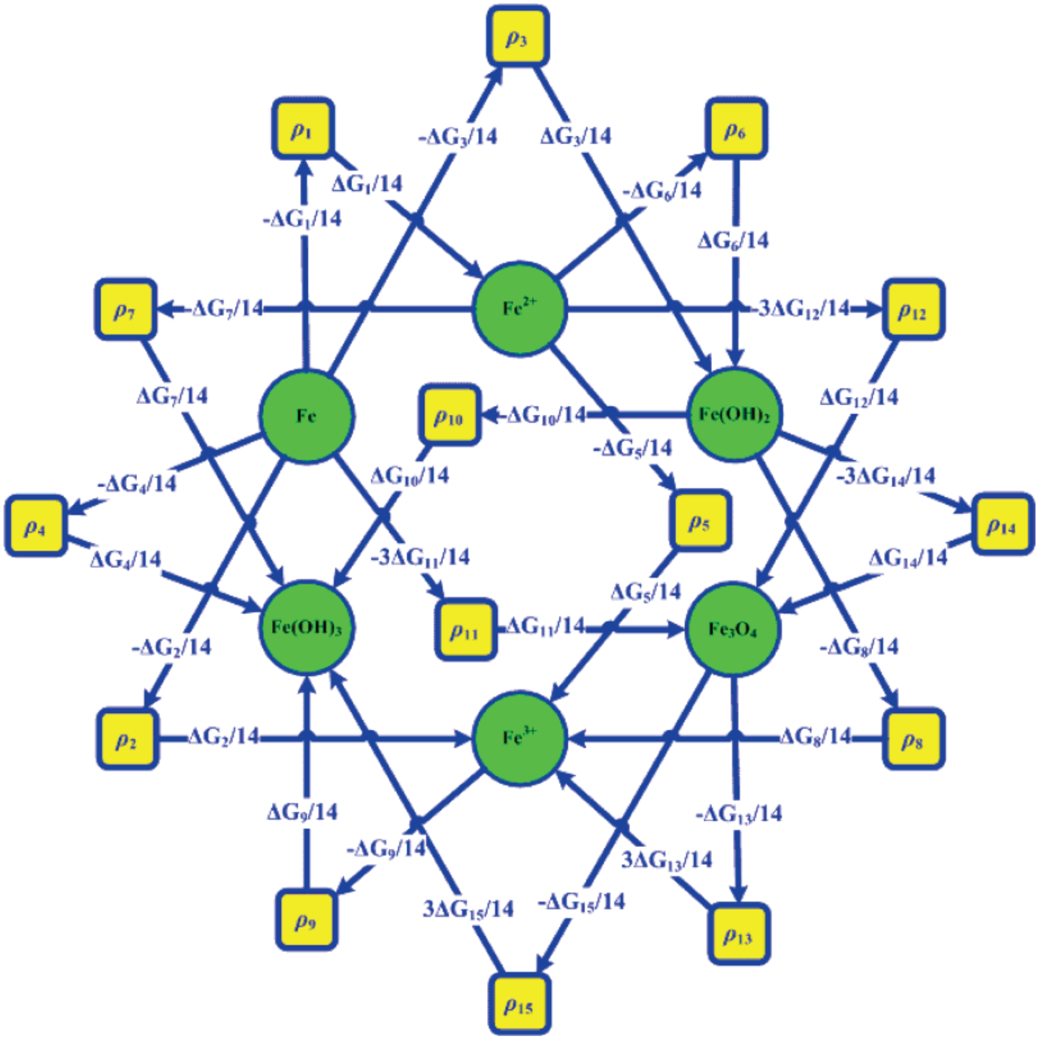

FIGURE 4. Bipartite graph interpretation of the overall stability in the system $e^-(aq) - H^+(aq) - H_2O(l) - Fe(s) - Fe^{2+}(aq) - Fe^{3+}(aq) - Fe(OH)_2(s) - Fe(OH)_3(s) - Fe_3O_4(s)$.

the determination of the RERs that dominate the stability relations under given conditions of pH and *E*.

Discussion

Stability relations in multiple redox reaction systems comprising one element are conventionally generated on the basis of the thermodynamic analysis of a certain class of reactions involving in a combinatorial manner all pairs of species comprising the system. In fact, this implies that the stability relations in a complex system are additive in that the stability relations may be partitioned into a linear sum of contributions coming from individual redox reactions. These reactions are stoichiometrically unique and are identical to RERs that have been deduced from chemical thermodynamics. Adopting a new quantitative definition of the stability of the species referred to as the overall stability and employing the concept of stoichiometric uniqueness in a complex chemical reaction system we have shown that stability relations may be indeed partitioned into a sum of contributions coming from RERs. We thus arrive at an exact and stoichiometrically unique formulation of stability relations in multiple chemical reaction systems. This new fundamental result leads to a simple and thermodynamically rigorous principle in constructing overall Pourbaix diagrams. Namely, a species is dominant if its overall stability is nonpositive and lower than the overall stabilities of the remaining species. Concomitantly, the overall stability approach allows a deeper insight into the main assumptions of the conventional stability analysis in electrochemical systems. As well-known, according to the conventional approach a species is stable if the Gibbs free energies of all reactions involving this particular species are strictly negative. For systems in which the number of atoms of the element M is equal to one in every species comprising the system, the overall and conventional Pourbaix diagrams coincide. If, at least, in one species the number of atoms of the element M is different from one, the two types of Pourbaix diagram may differ.

From the detailed analysis presented in this work it follows that both the conventional and overall stability analyses employ essentially the same set of reactions, i.e., RERs. The two approaches, however, differ in defining the stability field of a species. In this respect, the conventional approach may be regarded as more qualitative in that the absolute values of the Gibbs free energies of the RERs are not important. Thus, if the Gibbs free energy of at least one RER is not favorable toward the formation of a given species, the species is considered unstable regardless of the values of the Gibbs free energies of the remaining RERs. On the contrary, within the overall stability approach, a species may be stable even if the Gibbs free energies of some RERs are thermodynamically not favorable toward the production of this species provided the Gibbs free energies of the remaining RERs may overcome the deficit in Gibbs free energy. As a result, the overall stability analysis provides a quantitative and thermodynamically meaningful criterion for generating the predominance lines and triple points.

The difference between the overall and conventional approach is much deeper in systems involving simultaneously two or more different elements. A detailed analysis of these systems, however, requires a separate analysis and will be presented elsewhere.

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