A NEW METHOD OF COMPUTING MULTI-COMPONENT E-pH DIAGRAMS

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Abstract Aqueous E-pH Diagram is an essential tool for analyzing hydrometallurgical and corrosion processes. Due to the requirements for environmental protection and energy saving in recent years, waste water processing and hydrometallurgical process of concentrate have been greatly developed. The construction of E-pH diagrams has turned to multi-component systems. However, there are some limits in plotting such diagrams. There is only one diagram for one multi-component system, which can not reflect the truth of the aqueous reaction. In the paper, a new computation method is proposed to construct E-pH diagrams. Component activity term is used to determine the boundary of stable areas. For the multi-component systems, different atom ratios of elements have been taken into account. M-S-H2O system is chosen to study since it is of importance in metallurgical solution. Compared with conventional methods, the algorithm is simple and conforms to real conditions.

Key words: computation algorithm of E-pH diagrams; component activity term; M-H2O system; M-S-H2O system; atom ratios

1 THE COMPUTATION METHODS OF E-pH DIAGRAMS

1.1 Algorithm for Computing M-H2O System

In stead of considering the binary reactions between A and B for all the species, this approach is to consider the base reactions of all the species from the base component of the system.

As to M-H2O system, to consider any possible component MiHj-O~, we can use the following general reaction:

\[ M + wH_2O + mH^+ + ne = rM_iH_jO_~(q) \] (1)

where, \( i \neq 0 \), \( r = \frac{1}{i}, w = k/i, m = \frac{j-2k}{i}, n = \frac{j-2k-q}{i} \).

Nernst formula can be expressed as:

\[ -nFE = \Delta G^\circ + RT\ln(a(M_iH_jO_~)) - mRT\ln(a(H^+)) - wRT\ln(a(H_2O)) \] (2)

With \( a(H_2O) = 1 \), equation (2) can be simplified as:

\[ E = -\frac{\Delta G^\circ}{nF} - \frac{RT}{nF}\ln(a(M_iH_jO_~)) - \frac{2.303mRT}{nF}pH \] (3)

The component activity term would be

\[ \text{lg}(a(M_iH_jO_~))' = -\frac{\Delta G^\circ}{2.303RT} - \frac{nF}{2.303RT}E - mpH \] (4)

Due to the decrease of high-grade ores, low-grade ores are commonly mined and hydrometallurgical processes become more important. Besides, environment protection gives new challenges to industrial wastewater. As an important theoretical tool, E-pH diagram for simple metalwater system is extended to multi-component systems to satisfy new requirements.

The potential diagram in essence is one type of thermodynamic diagram, which translates thermodynamic data to diagrams. It is very repetitive and tedious, so that the application of computer to calculating and plotting such diagrams is always a great task for research workers [1-7]. However, being restricted to traditional methods, there is still some limits in plotting multi-component diagrams. Atom ratio of elements is seldom taken into account and the first element is regarded as the main one and the others are considered as accessory ones. Wadsley [8] pointed out this problem and plotted the diagrams of Fe-S-H2O system with different atom ratios of S/Fe. But no details and algorithms for such diagrams were illustrated.

In the present paper, a new method, component activity term method is proposed to plot E-pH diagram. The algorithm solved the problem of different atom ratio, so that the diagrams conform to the actual condition better.
Expressed as the following general equation:

\[ \lg(a(M\text{H}_2\text{O}))' = A\text{pH} + BE + C \]  

where, \( A = -m, B = -nF/(2.303RT), C = -\Delta G^0/(2.303RT). \)

From equation (5), it is known that, at any specified point \((E, \text{pH})\), all the component activity terms can be calculated. The species with the maximum activity term is taken as the most stable species because the free energy of equation (1) is the lowest and the tendency of the reaction is the largest.

The equilibrium lines between two species \(M\text{H}_2\text{O} \_1, M\text{H}_2\text{O} \_2\) can be obtained from

\[ \lg(a(M\text{H}_2\text{O} \_1)) = \lg(a(M\text{H}_2\text{O} \_2)) \]  

in addition to the condition of no third species with a larger activity term on the line. An invariant point exists among three species \(M\text{H}_2\text{O} \_1, M\text{H}_2\text{O} \_2, M\text{H}_2\text{O} \_3\) when

\[ \lg(a(M\text{H}_2\text{O} \_1)) = \lg(a(M\text{H}_2\text{O} \_2)) = \lg(a(M\text{H}_2\text{O} \_3)) \]  

under the condition that there is no other species with a larger activity term at the point. All the invariant points can be determined by solving the equations groups and the whole E-pH diagram can be completed by joining all the points.

1.2 E-pH Diagram of M-H\textsubscript{2}O System at Specified Component Activity

The above component activity term is deduced, regarding the actual activity as unit. Assuming the activity of species \(X\) is \(A_X\), there is some change for the expression of activity term. Subtracting the real activity term \(\lg(A_X)\) from both sides of equation (4), the general activity term at different values of \([A_X]\) is,

\[ \lg([A_X])' = A\text{pH} + BE + C, \]

\[ C = -\Delta G^0/2.303RT - r\lg A_X \]

It can be explained as follows for the most stable component of the stable area. To the species with specific activity, there is some specific area on the E-pH diagram, where its calculated activity value can reach or exceed its specific activity value and the activity term is the largest among all the species with the same calculation.

1.3 The Algorithm for Plotting E-pH Diagram of M-S-H\textsubscript{2}O System

Traditionally, people always regard S as an accessory element when plot the E-pH diagrams of M-S-H\textsubscript{2}O system. In essence it is regarded that the system is sulfur-rich. Suppose a simple chemical reaction:

\[ aA + bB = cC \]

If the reaction is complete and the quantity of \(B\) is greater than chemical stoichiometric one, then the predominant species is \(C + B\), otherwise the predominant species is \(C + A\). Thus the ratio of \(A\) to \(B\) determines which species \(C\) will coexist with. Such situation is always true. For example, Tang Motang\([9]\) developed a new chlorination-hydrolization process to leach various antimony ores. The A\textsuperscript{*} leachant is composed of Sb\textsuperscript{5+} and Cl\textsuperscript{-}. The system is Sb-rich instead of S-rich. So the traditional E-pH diagram is not complete. A complete algorithm is described in the following.

To illustrate more clearly, we use the following definition. Pure M-type species means M-bearing species which includes only element M (elements H, O are certainly included, the following is the same.). Pure S-type species means species which includes only element S. MS-type M-bearing species means M-bearing species which includes M and S. MS-type S-bearing species points S-bearing species which includes M and S. So M-bearing species includes pure M-bearing species and MS-type M-bearing species. And S-bearing species includes pure S-bearing species and MS-type S-bearing species.

To the M-S-H\textsubscript{2}O system, the base elements are M and S. At first we consider M-H\textsubscript{2}O and S-H\textsubscript{2}O two single systems.

The general reaction equation for the pure M-bearing species can be expressed as,

\[ M + w_1H_2O + m_1H^+ + n_1e = r_1M\text{H}_2\text{O} \_1(q_1) \]  

For the pure S-bearing species,

\[ S + w_2H_2O + m_2H^+ + n_2e = r_2S\text{H}_2\text{O} \_2(q_2) \]

Suppose at any point \((E, \text{pH})\), the most stable pure M-bearing species and S-bearing species are \(M\text{H}_2\text{O} \_1\) and \(S\text{H}_2\text{O} \_2\), respectively. Then the base reaction equation for the M-bearing species is,

\[ j3S\text{H}_2\text{O} \_2 + w_3H_2O + m_3H^+ + n_3e = r_3M\text{H}_2\text{O} \_3 + L(q_3) \]

Identically, it is for the S-bearing species,

\[ S + j4M\text{H}_2\text{O} \_1 + w_4H_2O + m_4H^+ + n_4e = r_4S\text{H}_2\text{O} \_3 + L(q_4) \]

All the coefficients of the above equations can be easily balanced. Correspondingly, the activity term for the M-bearing species is,

\[ \lg([A_X])' = A\text{pH} + BE + C, \]

And for the S-bearing species is,

\[ \lg([A_X])' = A\text{pH} + B_2E + C_2 \]

At this point, the most stable species are one M-bearing species and one S-bearing species with respective maximum activity term.

With the same method, E-pH diagram for two-met-